Supplementary Information

Synthesis of *cis*-Fused Cyclopentenone-Pyrrolidine Scaffolds *via* Sequential *aza*-Piancatelli and Conia-ene Type Reactions in One-pot

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Table of Contents

1. General Information

All chemicals have been purchased from commercial sources and were used without further purification unless otherwise noted. All solvents are reagent grade or HPLC grade. The synthetic transformations have been monitored by thin layer chromatography (TLC). TLC was performed on silica gel 60 F_{254} plates (glass plates). Concentration under reduced pressure was performed by rotary evaporation below 45 °C. Column chromatography was performed using silica gel (100-200 mesh) packed in glass columns. Yields refer to spectroscopically pure compounds after isolation. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ using 600 MHz (^{1}H), 500 MHz (^{1}H), 400 MHz (^{1}H), 300 MHz (^{1}H), 100 MHz (^{13}C), 125 MHz (^{13}C) and 377 MHz (^{19}F). Chemical shifts (δ-values) are reported in ppm, spectra were calibrated related to solvents' residual proton chemical shifts ($CDCl_3$, δ = 7.26) and solvents' residual carbon chemical shifts ($CDCl_3$, δ = 77.16 ppm), multiplicity is reported as follows: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, ddd= doublet of doublet of doublet, td = triplet of doublet, m = multiplet or unresolved and coupling constant *J* in Hz. Melting points (mp) were determined in open capillaries and are uncorrected. Infrared spectra (IR) were recorded on a 0.1 mm KBr demountable cell. High-resolution mass spectra (HRMS) were obtained by electrospray ionization using a Q-TOF mass spectrometer in positive ion mode (M+H) as indicated.

2. Experimental and Characterization of Compounds

2.1. General Procedure for Furfuryl Alcohols 1

Furfuryl Alcohols **1** were prepared according to literature precedent and spectral data were checked by matching the literature values.[1] To synthesize furfuryl alcohols **1**, to a solution of furan (1.4 mmol, 1.4 equiv) in anhydrous THF (20 mL) at -78 °C was added *n*-BuLi (1.2 mmol, 1.2 equiv). After, the resulting light yellow coloured solution was to stir for 1 h, then corresponding aldehyde (1.0 mmol, 1.0 equiv) in anhydrous THF (20 mL) was added to the reaction mixture in dropwise and the stirring was continued for 15 to 30 min at the same temperature. The reaction was then quenched by saturated aqueous NH_4Cl (10 mL) and was allowed to warm to room temperature. The reaction solvent (THF) was evaporated under reduced pressure and obtained crude residue was dissolved in EtOAc (2 x 20 mL) and washed with water (15 mL) followed by brine solution (15 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The crude product was purified by chromatography on silica gel to afford the furfuryl alcohols **1**.

2.2. General Procedure for *N*-propargyl anilines 2

N-Propargyl anilines **2** were prepared according to literature precedent and spectral data were checked by matching the literature values.[2] To synthesize *N*-propargyl anilines, propargyl bromide (2.00 mmol), K_2CO_3 (4.00 mmol), and an aniline derivative (8 mmol) were successively added to a distilled acetonitrile (2 mL) in a screw-capped tube under an N_2 atmosphere. The mixture was to stir at room temperature for 1-3 days. After the completion of reaction, reaction mixture was filtered off, the filtrate was evaporated under reduced pressure. The crude product was purified by a silica gel column chromatography (10% EtOAc/hexanes) to afford the corresponding *N*-propargyl anilines **2**.

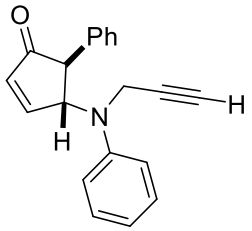
2.3. General Procedure for synthesis of *cis*-fused cyclopentenone-pyrrolidines 4

The reaction was performed with furyl alcohol **1** (1 equiv) and *N*-propargyl aniline **2** (1 equiv) in 1,4-dioxane (0.3 m) were added $B(C_6F_5)_3$ (10 mol%) and allowed to stir at 60 $^{\circ}$C until complete conversion of starting material (by TLC analysis). After complete conversion triethylamine (0.2 equiv), $Cu(OTf)_2$ (0.05 equiv) and TPP (0.2 equiv) were added sequentially. The reaction was allowed to stir at 90 $^{\circ}$C until completion of reaction. After completion of reaction, reaction mixture

was diluted by adding EtOAc, which filtered through celite. Further filtrate was concentrated and obtained crude was purified by silica gel column chromatography.

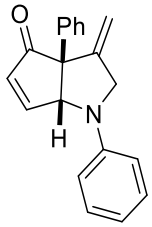
2.4 Experimental and Characterization of *cis*-fused cyclopentenone-pyrrolidines (3a, 4a-s)

4-(ethynyl(phenyl)amino)-5-phenylcyclopent-2-en-1-one (3a)



The reaction was performed with furan-2-yl(phenyl)methanol **1a** (0.100 g, 0.57 mol) and *N*-(prop-2-yn-1-yl)aniline **2a** (0.075 g, 0.57 mol) in 1,4-dioxane (2ml, 0.3 m) were added $B(C_6F_5)_3$ (0.029 g, 10 mol%) and allowed to stir at 60 °C until complete conversion of starting material (by TLC analysis) After completion of reaction, reaction mixture was filtered and crude residue was purified by silica gel column chromatography (10% EtOAc/hexanes) to afford **3a** (0.108 g, 66%) as white solid. mp. 134-136 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, J = 5.8, 2.4 Hz, 1H), 7.38 – 7.27 (m, 3H), 7.19 – 7.08 (m, 4H), 6.80 (t, J = 7.3 Hz, 1H), 6.74 (d, J = 8.0 Hz, 2H), 6.51 (dd, J = 5.8, 2.1 Hz, 1H), 5.14 (dd, J = 4.6, 2.2 Hz, 1H), 4.06 (dd, J = 18.4, 2.4 Hz, 1H), 3.92 (dd, J = 18.4, 2.2 Hz, 1H), 3.74 (d, J = 2.9 Hz, 1H), 2.28 (t, J = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 162.4, 147.4, 138.3, 135.7, 129.3, 129.2, 128.3, 127.5, 119.6, 115.4, 81.1, 73.0, 69.4, 57.1, 36.9. IR (thin film) ν_{max} (cm^{-1}) 3310, 3064, 2180, 1672, 1607, 1479, 1342, 1280, 1167, 1120, 751, 656. HRMS (ESI) m/z $[M+H]^+$ calculated for $C_{20}H_{18}NO$ 288.1388, found 288.1398.

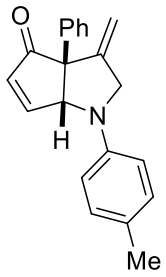
3-Methylene-1,3a-diphenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4a)



By following the general procedure, the reaction was performed with furan-2-yl(phenyl)methanol **1a** (0.100 g, 0.57 mol) and *N*-(prop-2-yn-1-yl)aniline **2a** (0.075 g, 0.57 mol) in 1,4-dioxane (2 ml, 0.3m) were added $B(C_6F_5)_3$ (0.029 g, 10 mol%) and allowed to stir at 60 °C until complete

conversion of starting material (by TLC analysis). To reaction mixture triethylamine (24 µl, 0.3 equiv), $Cu(OTf)_2$ (10 mg, 0.05 equiv) and TPP (30 mg, 0.2 equiv) were added sequentially. The reaction was allowed to stir at 90 °C until completion of reaction. After completion of reaction, reaction mixture was filtered and crude residue was purified by silica gel column chromatography (10% EtOAc/hexanes) to afford **4a** (0.14 g, 74%) as colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (dd, J = 5.8, 1.8 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.34 – 7.23 (m, 5H), 6.80 (t, J = 7.3 Hz, 1H), 6.69 (d, J = 7.9 Hz, 2H), 6.33 (dd, J = 5.8, 0.9 Hz, 1H), 5.42 (dt, J = 11.6, 2.2 Hz, 2H), 5.18 (s, 1H), 4.39 (dt, J = 13.9, 2.3 Hz, 1H), 4.12 (dt, J = 13.8, 2.1 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 158.4, 145.6, 145.1, 134.2, 129.8, 128.8, 127.4, 127.4, 117.7, 112.7, 112.5, 74.6, 65.1, 54.0. IR (thin film) ν_{max} (cm^{-1}) 3391, 3064, 1712, 1607, 1481, 1340, 1282, 1166, 1125, 755, 659. HRMS (ESI) m/z $[M+H]^+$ calculated for $C_{20}H_{18}NO$ 288.1388, found 288.1379.

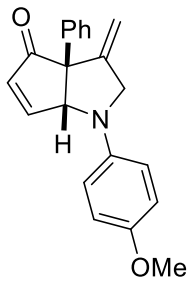
3-Methylene-3a-phenyl-1-(*p*-tolyl)-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4b)



By following the general procedure, the reaction was performed with furan-2-yl(phenyl)methanol **1a** (0.100 g, 0.57 mol) and 4-methyl-*N*-(prop-2-yn-1-yl)aniline **2b** (0.082 g, 0.57 mol) in 1,4-dioxane (2 ml, 0.3m) were added $B(C_6F_5)_3$ (0.029 g, 10 mol%) and allowed to stir at 60 °C until complete conversion of starting material (by TLC analysis). To reaction mixture triethylamine (24 µl, 0.3 equiv), $Cu(OTf)_2$ (10 mg, 0.05 equiv) and TPP (30 mg, 0.2 equiv) were added sequentially. The reaction was allowed to stir at 90 °C until completion of reaction. After completion of reaction, reaction mixture was filtered and crude residue was purified by silica gel column chromatography (10% EtOAc/hexanes) to afford **4b** (0.139 g, 81%) as off-white semi-solid. ^{1}H NMR (500 MHz, CDCl3) δ 7.74 (dd, J = 5.8, 1.7 Hz, 1H), 7.40 – 7.25 (m, 5H), 7.10 (d, J = 8.3 Hz, 2H), 6.62 (d, J = 8.3 Hz, 2H), 6.32 (dd, J = 5.8, 0.6 Hz, 1H), 5.47 – 5.38 (m, 2H), 5.15 (s, 1H), 4.36 (dt, J = 13.8, 1.9 Hz, 1H), 4.08 (dt, J = 13.8, 1.9 Hz, 1H), 2.27 (s, 3H). ^{13C} NMR (100 MHz, $CDCl_3$) δ 204.2, 158.6, 145.4, 143.6, 140.9, 134.2, 130.3, 128.8, 127.4, 127.4, 127.0, 112.7, 112.6, 74.8, 65.1, 54.0,

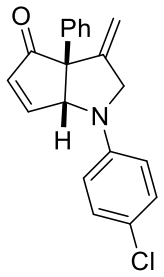
20.4. IR (thin film) ν_{max} (cm^{-1}) 3388, 3060, 1719, 1607, 1481, 1340, 1279, 1170, 1125, 754, 662; HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{21}H_{20}NO$ 302.1545, found 302.1539.

1-(4-Methoxyphenyl)-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4c)



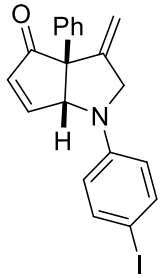
By following the general procedure, the reaction was performed with furan-2-yl(phenyl)methanol **1a** (0.100 g, 0.57 mol) and 4-methoxy-*N*-(prop-2-yn-1-yl)aniline **2c** (0.092 g, 0.57 mol) in 1,4-dioxane (2 ml, 0.3m) were added $B(C_6F_5)_3$ (0.029 g, 10 mol%) and allowed to stir at 60 °C until complete conversion of starting material (by TLC analysis). To reaction mixture triethylamine (24 µl, 0.3 equiv), $Cu(OTf)_2$ (10 mg, 0.05 equiv) and TPP (30 mg, 0.2 equiv) were added sequentially. The reaction was allowed to stir at 90 °C until completion of reaction. After completion of reaction, reaction mixture was filtered and crude residue was purified by silica gel column chromatography (10% EtOAc/hexanes) to afford **4c** (0.123 g, 68%) as pale yellow semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 5.8 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.35 – 7.28 (m, 2H), 7.26 (d, J = 1.0 Hz, 1H), 6.89 (d, J = 9.0 Hz, 2H), 6.66 (d, J = 9.0 Hz, 2H), 6.33 (dd, J = 5.8, 0.9 Hz, 1H), 5.48 – 5.35 (m, 2H), 5.12 (s, 1H), 4.38 – 4.27 (m, 1H), 4.04 (d, J = 13.5 Hz, 1H), 3.77 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 153.7, 142.0, 132.6, 128.1, 127.0, 113.6, 111.8, 110.2, 110.0, 106.0, 101.0, 67.3, 56.1, 35.9, 32.8, 21.1. IR (thin film) ν_{max} (cm^{-1}) 3380, 3064, 1713, 1600, 1480, 1320, 1275, 1150, 1115, 758, 638. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{21}H_{20}NO_2$ 318.1494, found 318.1490.

1-(4-Chlorophenyl)-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4d)



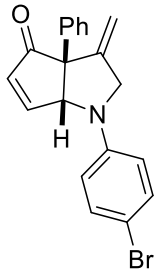
By following the general procedure, the reaction was performed with furan-2-yl(phenyl)methanol **1a** (0.100 g, 0.57 mol) and 4-chloro-*N*-(prop-2-yn-1-yl)aniline **2d** (0.114 g, 0.57 mol) in 1,4-dioxane (2 ml, 0.3m) were added $B(C_6F_5)_3$ (0.029 g, 10 mol%) and allowed to stir at 60 °C until complete conversion of starting material (by TLC analysis). To reaction mixture triethylamine (24 µl, 0.3 equiv), $Cu(OTf)_2$ (10 mg, 0.05 equiv) and TPP (30 mg, 0.2 equiv) were added sequentially. The reaction was allowed to stir at 90 °C until completion of reaction. After completion of reaction, reaction mixture was filtered and crude residue purified by silica gel column chromatography (10% EtOAc/hexanes) to afford **4d** (0.140 g, 77%) as brown semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dt, J = 8.4, 4.2 Hz, 1H), 7.41 – 7.32 (m, 4H), 7.28 – 7.19 (m, 3H), 6.69 – 6.57 (m, 2H), 6.35 (dd, J = 5.8, 0.9 Hz, 1H), 5.42 (dt, J = 8.7, 2.1 Hz, 2H), 5.12 (s, 1H), 4.35 (dt, J = 13.8, 2.2 Hz, 1H), 4.09 (dt, J = 13.8, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.7, 157.7, 144.6, 144.2, 140.5, 134.4, 129.5, 128.8, 127.5, 127.3, 122.6, 113.5, 112.9, 74.6, 65.1, 54.0. IR (thin film) ν_{max} (cm^{-1}) 3396, 3078, 1713, 1602, 1478, 1337, 1269, 1172, 1129, 990, 751, 674. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{20}H_{17}ClNO$ 322.0998, found 322.0979.

(4-Iodophenyl)-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4e)



By following the general procedure, the reaction was performed with furan-2-yl(phenyl)methanol **1a** (0.150 g, 0.86 mmol) and 4-iodo-*N*-(prop-2-yn-1-yl)aniline **2e** (0.221g, 0.861 mmol) in 1,4-dioxane (2 ml, 0.3m) were added $B(C_6F_5)_3$ (0.044 g, mol%) and allowed to stir at 75 ^oC until complete conversion of starting material (by TLC analysis). To reaction mixture triethylamine (24 µl, 0.3 equiv), $Cu(OTf)_2$ (0.015 g, 0.05 equiv) and TPP (45 mg, 0.2 equiv) were added sequentially. The reaction was allowed to stir at 90 ^oC until completion of reaction. After completion of reaction, reaction mixture was filtered and crude residue purified by silica gel column chromatography (10% EtOAc/hexanes) to afford orange solid **4e** (0.166 g, 70%). mp. 120 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 4.7 Hz, 1H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.30 (dt, *J* = 17.0, 6.7 Hz, 5H), 6.45 (d, *J* = 8.6 Hz, 2H), 6.32 (d, *J* = 5.7 Hz, 1H), 5.52 – 5.34 (m, 2H), 5.10 (s, 1H), 4.33 (d, *J* = 13.9 Hz, 1H), 4.07 (d, *J* = 13.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 203.7, 157.7, 145.1, 144.5, 140.5, 138.2, 134.4, 128.8, 127.5, 127.3, 114.7, 113.0, 78.8, 74.4, 65.04, 53.82. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{20}H_{17}NOI$ 414.0355, found 414.0336.

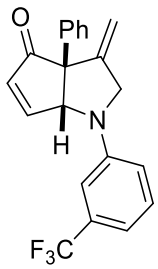
1-(4-Bromophenyl)-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4f)



By following the general procedure, the reaction was performed with furan-2-yl(phenyl)methanol **1a** (0.100 g, 0.57 mol) and 4-bromo-*N*-(prop-2-yn-1-yl)aniline **2f** (0.119 g, 0.57 mol) in 1,4-dioxane (2 ml, 0.3m) were added $B(C_6F_5)_3$ (0.029 g, 10 mol%) and allowed to stir at 60 ^oC until complete conversion of starting material (by TLC analysis). To reaction mixture triethylamine (24 µl, 0.3 equiv), $Cu(OTf)_2$ (10 mg, 0.05 equiv) and TPP (30 mg, 0.2 equiv) was added sequentially. The reaction was allowed to stir at 90 ^oC until completion of reaction. After completion of reaction, reaction mixture was filtered and crude residue was purified by silica gel column chromatography (10% EtOAc/hexanes) to afford **4f** (0.164 g, 79%) as yellow solid. mp. 195 ^oC. ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.73 – 7.63 (m, 1H), 7.41 – 7.31 (m, 6H), 7.28 – 7.22 (m, 1H), 6.54 (d, *J* = 9.0 Hz, 2H), 6.33 (dd, *J* = 5.8, 1.0 Hz, 1H), 5.41 (dt, *J* = 7.1, 2.2 Hz, 2H), 5.11 (s, 1H), 4.33 (dd, *J* = 9.2, 6.9

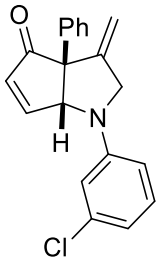
Hz, 1H), 4.07 (d, J = 13.9 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8, 157.7, 144.6, 140.5, 134.4, 132.4, 128.8, 127.5, 127.3, 114.1, 113.0, 109.7, 74.6, 65.1, 53.91. IR (thin film) ν_{max} (cm^{-1}) 3386, 3020, 1711, 1612, 1490, 1342, 1207, 1164, 1096, 754, 649. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{20}H_{17}BrNO$ 365.0493, found 366.0488

3-Methylene-3a-phenyl-1-(3-(trifluoromethyl)phenyl)-2,3,3a,6a-tetrahydrocyclopenta[*b*] pyrrol-4(1*H*)-one (4g)



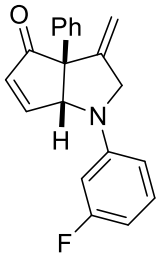
By following the general procedure, the reaction was performed with furan-2-yl(phenyl)methanol **1a** (0.100 g, 0.57 mol) and 3-trifluoromethyl-*N*-(prop-2-yn-1-yl)aniline **2g** (0.114 g, 0.57 mol) in 1,4-dioxane (2 ml, 0.3m) were added $B(C_6F_5)_3$ (0.029 g, 10 mol%) and allowed to stir at 60 °C until complete conversion of starting material (by TLC analysis). To reaction mixture triethylamine (24 µl, 0.3 equiv), $Cu(OTf)_2$ (10 mg, 0.05 equiv) and TPP (30 mg, 0.2 equiv) were added sequentially. The reaction was allowed to stir at 90 °C until completion of reaction. After completion of reaction, reaction mixture was filtered and crude residue purified by silica gel column chromatography (10% EtOAc/hexanes) to afford **4g** (0.166 g, 82%) as pale yellow semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 5.8, 1.8 Hz, 1H), 7.43 – 7.27 (m, 6H), 7.03 (d, J = 7.7 Hz, 1H), 6.84 (dd, J = 11.5, 3.2 Hz, 2H), 6.37 (dd, J = 5.8, 0.9 Hz, 1H), 5.45 (dt, J = 9.8, 2.1 Hz, 2H), 5.18 (s, 1H), 4.43 (dt, J = 13.9, 2.2 Hz, 1H), 4.16 (dt, J = 13.9, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 157.4, 145.6, 144.2, 140.3, 134.5, 132.0 (q, J = 31.8 Hz), 130.1, 128.8, 127.5, 127.3, 124.26 (q, J = 272.6 Hz), 115.3, 114.0, 114.0 (q, J = 3.6 Hz), 108.7 (q, J = 3.7 Hz), 74.5, 65.1, 53.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.11. IR (thin film) ν_{max} (cm^{-1}) 3395, 3055, 1711, 1612, 1480, 1340, 1282, 1166, 1125, 756, 659. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{21}H_{17}F_3NO$ 356.1262, found 356.1246.

(3-Chlorophenyl)-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4h)



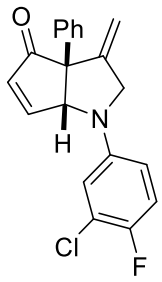
By following the general procedure, the reaction was performed with furan-2-yl(phenyl)methanol **1a** (0.100 g, 0.57 mol) and 3-chloro-*N*-(prop-2-yn-1-yl)aniline **2h** (0.114 g, 0.57 mol) in 1,4-dioxane (2 ml, 0.3m) were added $B(C_6F_5)_3$ (0.029 g, 10 mol%) and allowed to stir at 60 °C until complete conversion of starting material (by TLC analysis). To reaction mixture triethylamine (24 µl, 0.3 equiv), $Cu(OTf)_2$ (10 mg, 0.05 equiv) and TPP (30 mg, 0.2 equiv) were added sequentially. The reaction was allowed to stir at 90 °C until completion of reaction. After completion of reaction, reaction mixture was filtered and crude residue purified by silica gel column chromatography (10% EtOAc/hexanes) to afford **4h** (0.144 g, 78%) as off-white semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 5.8, 1.8 Hz, 1H), 7.36 – 7.30 (m, 4H), 7.29 – 7.24 (m, 1H), 7.18 (t, J = 8.1 Hz, 1H), 6.75 (dd, J = 7.9, 1.2 Hz, 1H), 6.65 (t, J = 2.1 Hz, 1H), 6.55 (dd, J = 8.3, 2.2 Hz, 1H), 6.34 (dd, J = 5.8, 0.9 Hz, 1H), 5.43 (dt, J = 6.5, 2.2 Hz, 2H), 5.12 (s, 1H), 4.37 (dt, J = 13.9, 2.3 Hz, 1H), 4.11 (dt, J = 13.9, 2.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.5, 157.5, 146.3, 144.1, 140.1, 135.3, 134.1, 130.4, 128.6, 127.2, 127.0, 117.3, 112.7, 112.1, 110.3, 74.2, 64.8, 53.6. IR (thin film) ν_{max} (cm^{-1}) 3382, 3069, 1708, 1620, 1486, 1219, 1163, 1120, 945, 762, 670. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{20}H_{17}NOCl$ 322.0999, found 322.0987.

(3-Fluorophenyl)-6a-methyl-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4i)



By following the general procedure, the reaction was performed with furan-2-yl(phenyl)methanol **1a** (0.100 g, 0.57 mmol) and 3-fluoro-*N*-(prop-2-yn-1-yl)aniline **2i** (0.085 g, 0.57 mmol) in 1,4-dioxane (2 ml, 0.3m) were added $B(C_6F_5)_3$ (0.029 g, 10 mol%) and allowed to stir at 75 ^oC until complete conversion of starting material (by TLC analysis). To reaction mixture triethylamine (24 µl, 0.3 equiv), $Cu(OTf)_2$ (0.010 g, 0.05 equiv) and TPP (0.045 g, 0.2 equiv) were added sequentially. The reaction was allowed to stir at 90 ^oC until completion of reaction. After completion of reaction, reaction mixture was filtered and crude residue purified by silica gel column chromatography (10% EtOAc/hexanes) to afford **4i** a**s** dark brown semi-solid (0.120 g, 66%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 5.8, 1.8 Hz, 1H), 7.43 – 7.27 (m, 5H), 7.26 – 7.16 (m, 1H), 6.54 – 6.41 (m, 2H), 6.38 – 6.29 (m, 2H), 5.43 (dt, J = 6.9, 2.2 Hz, 2H), 5.12 (s, 1H), 4.37 (dt, J = 13.9, 2.3 Hz, 1H), 4.12 (dt, J = 13.9, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.71, 164.22 (d, J = 243.9 Hz), 157.75, 147.17 (d, J = 10.6 Hz), 144.36, 140.37, 134.33, 130.79 (d, J = 10.2 Hz), 128.79, 127.46, 127.24, 112.93, 108.05, 104.16 (d, J = 21.4 Hz), 99.61 (d, J = 26.0 Hz), 74.53, 64.99, 53.96. ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.70. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{20}H_{17}NOF$ 306.1294, found 306.1298.

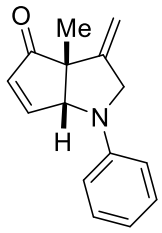
(3-Chloro-4-fluorophenyl)-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4j)



By following the general procedure, the reaction was performed with furan-2-yl(phenyl)methanol **1a** (0.100 g, 0.57 mol) and 3-chloro-4-fluoro-*N*-(prop-2-yn-1-yl)aniline **2j** (0.105 g, 0.57 mol) in 1,4-dioxane (2 ml, 0.3m) were added $B(C_6F_5)_3$ (0.029 g, 10 mol%) and allowed to stir at 75 ^oC until complete conversion of starting material (by TLC analysis). To reaction mixture triethylamine (24 µl, 0.3 equiv), $Cu(OTf)_2$ (0.010 g, 0.05 equiv) and TPP (0.030 g, 0.2 equiv) were added sequentially. The reaction was allowed to stir at 90 ^oC until completion of reaction. After completion of reaction, reaction mixture was filtered and crude residue purified by silica gel

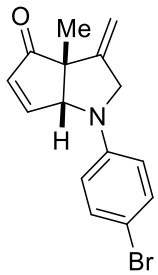
column chromatography (10% EtOAc/hexanes) to afford **4j** a**s** brown semi-solid (0.120 g, 60%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J = 5.8, 1.8 Hz, 1H), 7.34 (dd, J = 6.6, 3.3 Hz, 4H), 7.26 (s, 1H), 7.06 (t, J = 8.8 Hz, 1H), 6.66 (dd, J = 5.9, 3.0 Hz, 1H), 6.50 (dt, J = 9.0, 3.3 Hz, 1H), 6.36 (dd, J = 5.8, 0.9 Hz, 1H), 5.43 (dt, J = 10.6, 2.1 Hz, 2H), 5.08 (s, 1H), 4.33 (dt, J = 13.7, 2.2 Hz, 1H), 4.07 (dt, J = 13.7, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 151.2 (d, J = 239.0 Hz), 150.0, 144.4, 142.6, 140.3, 134.6, 128.8, 127.5, 127.2, 121.8 (d, J = 18.7 Hz), 117.3 (d, J = 22.0 Hz), 113.7, 113.1, 111.4 (d, J = 6.1 Hz), 74.79, 65.10, 54.05.^{19}F NMR (377 MHz, $CDCl_3$) δ -130.88. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{20}H_{16}NOFCl$ 340.0904, found 340.0893.

3a-Methyl-3-methylene-1-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4k)



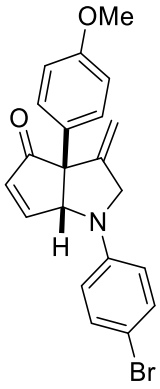
By following the general procedure, the reaction was performed with 1-(furan-2-yl)ethan-1-ol **1b** (0.100 g, 0.89 mol) and *N*-(prop-2-yn-1-yl)aniline **2a** (0.100g, 0.89 mol) in 1,4-dioxane (3 ml, 0.3m) were added $B(C_6F_5)_3$ (0.029 g, 10 mol%) and allowed to stir at 60 ˚C until complete conversion of starting material (by TLC analysis). To reaction mixture triethylamine (37 µl, 0.3equiv), $Cu(OTf)_2$ (0.016 g, 0.05 equiv) and TPP (0.046 g, 0.2 equiv) were added sequentially. The reaction was allowed to stir at 90 ˚C until completion of reaction. After completion of reaction, reaction mixture was filtered and crude residue purified by silica gel column chromatography (10% EtOAc/hexanes) to afford **4k** (0.104 g, 52%) as yellow semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, J = 5.8, 1.8 Hz, 1H), 7.40 – 7.27 (m, 2H), 6.81 (dd, J = 10.6, 4.1 Hz, 1H), 6.73 – 6.67 (m, 2H), 6.23 (dd, J = 5.8, 0.7 Hz, 1H), 5.30 (t, J = 2.3 Hz, 1H), 5.16 (t, J = 2.0 Hz, 1H), 4.84 (d, J = 0.7 Hz, 1H), 4.23 (dt, J = 13.9, 2.0 Hz, 1H), 3.91 (dt, J = 13.9, 2.3 Hz, 1H), 1.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.8, 157.7, 147.0, 145.7, 133.7, 129.6, 117.5, 112.6, 108.9, 71.7, 56.6, 52.7, 21.2. IR (thin film) ν_{max} (cm^{-1}) 3352, 3044, 1718, 1605, 1481, 1340, 1278, 1166, 1125, 659. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{15}H_{16}NO$ 226.1232, found 226.1226.

1-(4-Bromophenyl)-3a-methyl-3-methylene-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4l)



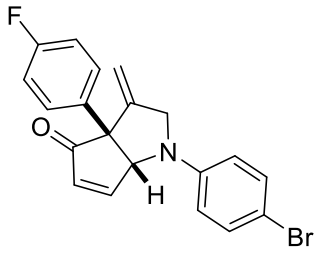
By following the general procedure, the reaction was performed with 1-(furan-2-yl)ethan-1-ol **1b** (0.100 g, 0.89 mol) and 4-bromo-*N*-(prop-2-yn-1-yl)aniline **2f** (0.186 g, 0.89 mol) in 1,4-dioxane (3 ml, 0.3m) were added $B(C_6F_5)_3$ (0.045 g, 10 mol%) and allowed to stir at 60 °C until complete conversion of starting material (by TLC analysis). To reaction mixture triethylamine (36 µl, 0.3equiv), $Cu(OTf)_2$ (0.016 g, 0.05 equiv) and TPP (0.046 g, 0.2 equiv) were added sequentially. The reaction was allowed to stir at 90 °C until completion of reaction. After completion of reaction, reaction mixture was filtered and crude residue purified by silica gel column chromatography (10% EtOAc/hexanes) to afford **4l** (0.099 g, 57%) as pale yellow semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, J = 5.8, 1.8 Hz, 1H), 7.42 – 7.32 (m, 2H), 6.66 – 6.52 (m, 2H), 6.24 (t, J = 7.2 Hz, 1H), 5.31 (t, J = 2.3 Hz, 1H), 5.16 (t, J = 2.0 Hz, 1H), 4.78 (s, 1H), 4.18 (ddd, J = 13.9, 6.6, 4.1 Hz, 1H), 3.87 (dt, J = 13.9, 2.3 Hz, 1H), 1.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.6, 157.1, 146.6, 144.8, 134.1, 132.5, 114.3, 109.7, 109.4, 71.8, 56.7, 52.9, 21.3. IR (thin film) ν_{max} (cm^{-1}) 3381, 3064, 1716, 1607, 1481, 1340, 1282, 1166, 1125, 992, 730, 689. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{15}H_{15}BrNO$ 304.0337, found 304.0327.

1-(4-Bromophenyl)-3a-(4-methoxyphenyl)-3-methylene-2,3,3a,6a-tetrahydrocyclopenta[*b*] pyrrol-4(1*H*)-one (4m)



By following the general procedure, the reaction was performed with (4-((oxidaneyl)-l5-methyl)phenyl)(furan-2-yl)methanol **1c** (0.100 g, 0.49 mol) and 4-bromo-*N*-(prop-2-yn-1-yl)aniline **2f** (0.102 g, 0.49 mol) in 1,4-dioxane (1.5 ml, 0.3m) were added $B(C_6F_5)_3$ (0.029 g, 10 mol%) and allowed to stir at 60 °C until complete conversion of starting material (by TLC analysis). To reaction mixture triethylamine (19 µl, 0.3 equiv), $Cu(OTf)_2$ (0.009 g, 0.05 equiv) and TPP (0.026 g, 0.2 equiv) were added sequentially. The reaction was allowed to stir at 90 °C until completion of reaction. After completion of reaction, reaction mixture was filtered and crude residue purified by silica gel column chromatography (10% EtOAc/hexanes) to afford **4m** (0.156 g, 81%) as yellow semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 5.9, 1.8 Hz, 1H), 7.36 (d, J = 9.0 Hz, 2H), 7.34 – 7.19 (m, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.65 – 6.50 (m, 2H), 6.34 (dd, J = 5.9, 0.9 Hz, 1H), 5.40 (dt, J = 9.0, 2.1 Hz, 2H), 5.08 (s, 1H), 4.33 (dt, J = 13.9, 2.2 Hz, 1H), 4.06 (dt, J = 13.9, 2.1 Hz, 1H), 3.78 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 158.9, 157.6, 145.0, 144.7, 134.5, 132.4, 128.5, 114.2, 114.1, 112.8, 109.7, 74.6, 64.6, 55.4, 53.9. IR (thin film) ν_{max} (cm^{-1}) 3391, 3064, 1712, 1607, 1481, 1380, 1212, 1166, 1125, 755, 659. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{21}H_{19}BrNO_2$ 396.0599, found 396.0565.

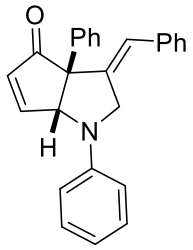
(4-Bromophenyl)-3a-(4-fluorophenyl)-3-methylene-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4n)



By following the general procedure, the reaction was performed with (4-fluorophenyl)(furan-2-yl)methanol **1d** (0.100 g, 0.52 mmol) and 4-bromo-*N*-(prop-2-yn-1-yl)aniline **2f** (0.109 g, 0.52 mmol) in 1,4-dioxane (2 ml, 0.3m) were added $B(C_6F_5)_3$ (0.027 g, 10 mol%) and allowed to stir at 75 °C until complete conversion of starting material (by TLC analysis). To reaction mixture triethylamine (22 µl, 0.3 equiv), $Cu(OTf)_2$ (0.010 mg, 0.05 equiv) and TPP (0.028 g, 0.2 equiv) were added sequentially. The reaction was allowed to stir at 90 °C until completion of reaction. After completion of reaction, reaction mixture was filtered and crude residue purified by silica gel column chromatography (10% EtOAc/hexanes) to afford **4n** as dark brown semi-solid (0.130 g,

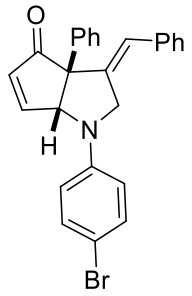
65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 5.8, 1.5 Hz, 1H), 7.49 – 7.29 (m, 4H), 7.01 (t, J = 8.6 Hz, 2H), 6.57 (d, J = 8.8 Hz, 2H), 6.35 (d, J = 5.8 Hz, 1H), 5.40 (d, J = 15.6 Hz, 2H), 5.08 (s, 1H), 4.34 (d, J = 13.9 Hz, 1H), 4.06 (d, J = 13.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.4, 162.0 (d, J = 246.8 Hz), 157.5, 144.8, 144.4, 136.2, 134.4, 132.4, 129.0 (d, J = 8.0 Hz), 115.6 (d, J = 21.4 Hz), 114.1, 113.0, 109.9, 74.4, 64.4, 53.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -114.91. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{20}H_{16}NOBrF$ 384.0383, found 384.0393

3-((Z)-Benzylidene)-1,3a-diphenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4o)



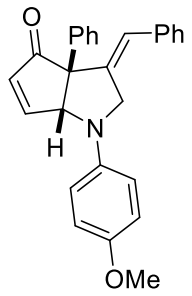
By following the general procedure, the reaction was performed with furan-2-yl(phenyl)methanol **1a** (0.100 g, 0.57 mol) and *N*-(3-phenylprop-2-yn-1-yl)aniline **2k** (0.117 g, 0.57 mol) in 1,4-dioxane (2 ml, 0.3m) were added $B(C_6F_5)_3$ (0.029 g, 10 mol%) and allowed to stir at 75ºC until complete conversion of starting material (by TLC analysis). To reaction mixture triethylamine (24 µl, 0.3 equiv), $Cu(OTf)_2$ (0.010 g, 0.05 equiv) and TPP (0.030 g, 0.2 equiv) were added sequentially. The reaction was allowed to stir at 90 ºC until completion of reaction. After completion of reaction, reaction mixture was filtered and crude residue purified by silica gel column chromatography (10% EtOAc/hexanes) to afford **4o** (0.152 g, 73%) as white solid. mp. 87-88 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, J = 5.8, 1.8 Hz, 1H), 7.43 – 7.37 (m, 4H), 7.37 – 7.27 (m, 8H), 6.86 – 6.77 (m, 3H), 6.72 (t, J = 2.4 Hz, 1H), 6.40 (dd, J = 5.8, 0.9 Hz, 1H), 5.18 (s, 1H), 4.74 (dd, J = 14.8, 2.5 Hz, 1H), 4.39 (dd, J = 14.8, 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.2, 145.3, 141.5, 137.4, 136.5, 134.6, 129.7, 128.8, 128.7, 128.7, 128.1, 127.6, 127.5, 117.7, 112.5, 73.3, 66.1, 52.3. IR (thin film) ν_{max} (cm^{-1}) 3385, 3060, 1715, 1607, 1481, 1340, 1282, 1166, 1125, 758, 662. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{26}H_2NO$ 364.1701, found 364.1706.

3-((*Z*)-Benzylidene)-1-(4-bromophenyl)-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4p)



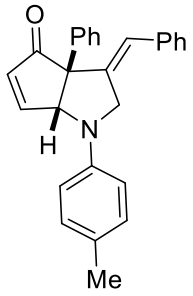
By following the general procedure, the reaction was performed with furan-2-yl(phenyl)methanol **1a** (0.100 g, 0.57 mol) and 4-bromo-*N*-(3-phenylprop-2-yn-1-yl)aniline **2l** (0.114 g, 0.57 mol) in 1,4-dioxane (2 ml, 0.3m) were added $B(C_6F_5)_3$ (0.029 g, 10 mol%) and allowed to stir at 75 ^oC until complete conversion of starting material (by TLC analysis). To reaction mixture triethylamine (24 µl, 0.3 equiv), $Cu(OTf)_2$ (0.010 g, 0.05 equiv) and TPP (0.030 g, 0.2 equiv) were added sequentially. The reaction was allowed to stir at 90 ^oC until completion of reaction. After completion of reaction, reaction mixture was filtered and crude residue purified by silica gel column chromatography (10% EtOAc/hexanes) to afford **4p** (0.203 g, 80%) as white solid. mp. 199-201 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 5.8, 1.7 Hz, 1H), 7.42 – 7.36 (m, 6H), 7.35 – 7.26 (m, 6H), 6.72 (t, J = 2.4 Hz, 1H), 6.65 (d, J = 8.9 Hz, 2H), 6.40 (d, J = 6.4 Hz, 1H), 5.12 (s, 1H), 4.67 (dd, J = 14.7, 2.5 Hz, 1H), 4.35 (dd, J = 14.7, 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.0, 157.5, 144.4, 141.5, 136.9, 136.4, 134.9, 132.5, 128.9, 128.8, 128.5, 127.8, 127.6, 127.6, 114.2, 109.9, 73.4, 66.2, 52.5. IR (thin film) ν_{max} (cm^{-1}) 3391, 3064, 1719, 1607, 1481, 1338, 1279, 1176, 1145, 760, 662. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{26}H_{21}BrNO$ 442.0807, found 442.0790.

3-((*Z*)-Benzylidene)-1-(4-methoxyphenyl)-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4q)



By following the general procedure, the reaction was performed with furan-2-yl(phenyl)methanol **1a** (0.100 g, 0.57 mol) and 4-methoxy-*N*-(3-phenylprop-2-yn-1-yl)aniline **2m** (0.136 g, 0.57 mol) in 1,4-dioxane (2 ml, 0.3m) were added $B(C_6F_5)_3$ (0.029 g, 10 mol%) and allowed to stir at 75 ^oC until complete conversion of starting material (by TLC analysis). To reaction mixture triethylamine (24 µl, 0.3 equiv), $Cu(OTf)_2$ (0.010 g, 0.05 equiv) and TPP (0.030 g, 0.2 equiv) were added sequentially. The reaction was allowed to stir at 90 ^oC until completion of reaction. After completion of reaction, reaction mixture was filtered and crude residue purified by silica gel column chromatography (10% EtOAc/hexanes) to afford **4q** as yellow solid (0.124 g, 55%). mp. 171 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 5.9, 1.7 Hz, 1H), 7.44 – 7.39 (m, 4H), 7.37 – 7.26 (m, 6H), 6.97 – 6.89 (m, 2H), 6.79 – 6.72 (m, 2H), 6.68 (d, J = 2.3 Hz, 1H), 6.39 (dd, J = 5.9, 0.7 Hz, 1H), 5.12 (s, 1H), 4.67 (dd, J = 14.5, 2.4 Hz, 1H), 4.30 (dd, J = 14.5, 2.5 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.4, 158.3, 152.3, 141.8, 140.0, 138.0, 136.7, 134.9, 128.8, 128.8, 128.7, 128.2, 127.7, 127.6, 127.4, 115.5, 113.8, 74.0, 66.3, 56.0, 52.5. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{27}H_{24}O_2N$ 394.1797, found 394.1801.

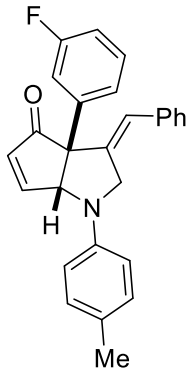
3-((*Z*)-Benzylidene)-3a-phenyl-1-(*p*-tolyl)-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*) one (4r)



By following the general procedure, the reaction was performed with furan-2-yl(phenyl)methanol **1a** (0.100 g, 0.57 mmol) and 4-methyl-*N*-(3-phenylprop-2-yn-1-yl)aniline **2n** (0.127 g, 0.57 mmol) in 1,4-dioxane (2 ml, 0.3m) were added $B(C_6F_5)_3$ (0.029 g, 10 mol%) and allowed to stir at 75 ^oC until complete conversion of starting material (by TLC analysis). To reaction mixture triethylamine (24 µl, 0.3 equiv), $Cu(OTf)_2$ (0.010 g, 0.05 equiv) and TPP (0.030 g, 0.2 equiv) were added sequentially. The reaction was allowed to stir at 90 ^oC until completion of reaction. After completion of reaction, reaction mixture was filtered and crude residue purified by silica gel column chromatography (10% EtOAc/hexanes) to afford **4r** as pale yellow (0.142 g, 65%). mp.

190-192 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 5.8 Hz, 1H), 7.38 (d, J = 4.8 Hz, 4H), 7.35 – 7.25 (m, 6H), 7.12 (d, J = 8.3 Hz, 2H), 6.70 (d, J = 8.1 Hz, 3H), 6.37 (d, J = 5.8 Hz, 1H), 5.14 (s, 1H), 4.69 (dd, J = 14.7, 2.0 Hz, 1H), 4.34 (dd, J = 14.7, 1.9 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.4, 158.3, 143.3, 141.8, 137.8, 136.6, 134.7, 130.3, 128.8, 128.8, 128.7, 128.2, 127.7, 127.6, 127.4, 112.7, 73.5, 66.9, 52.4, 20.5. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{27}H_{24}NO$ 378.1849, found 378.1852.

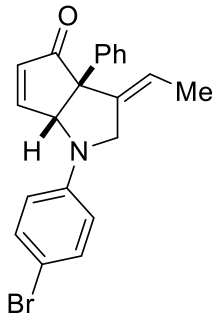
3-((*Z*)-Benzylidene)-3a-(3-fluorophenyl)-1-(*p*-tolyl)-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4s)



By following the general procedure, the reaction was performed with (3-fluorophenyl)(furan-2-yl)methanol **1a** (0.100 g, 0.52 mmol) and 4-methyl-*N*-(3-phenylprop-2-yn-1-yl)aniline **2o** (0.115 g, 0.52 mmol) in 1,4-dioxane (2 ml, 0.3m) were added $B(C_6F_5)_3$ (0.027 g, 10 mol%) and allowed to stir at 75 °C until complete conversion of starting material (by TLC analysis). To reaction mixture triethylamine (22 µl, 0.3 equiv), $Cu(OTf)_2$ (0.010 g, 0.05 equiv) and TPP (0.028 mg, 0.2 equiv) were added sequentially. The reaction was allowed to stir at 90 °C until completion of reaction. After completion of reaction, reaction mixture was filtered and crude residue purified by silica gel column chromatography (10% EtOAc/hexanes) to afford **4s** as dark brown semi-solid (0.114 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 5.8, 1.7 Hz, 1H), 7.40 (dd, J = 9.6, 5.7 Hz, 2H), 7.33 – 7.24 (m, 6H), 7.20 – 7.11 (m, 3H), 6.97 (ddd, J = 8.1, 2.4, 1.5 Hz, 1H), 6.83 – 6.65 (m, 3H), 6.38 (dd, J = 5.8, 0.7 Hz, 1H), 5.14 (s, 1H), 4.69 (dd, J = 14.8, 2.4 Hz, 1H), 4.32 (dd, J = 14.7, 2.5 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.5, 164.1, 162.89 (d, J = 246.1 Hz), 144.02 (d, J = 7.2 Hz), 143.1, 137.3, 136.3, 134.6, 130.3, 130.2, 128.7, 128.7, 128.4, 127.7, 127.2, 123.2, 114.9 (d, J = 22.8 Hz), 114.3 (d, J = 21.2 Hz), 112.7, 73.2, 65.6, 52.1, 20.4.

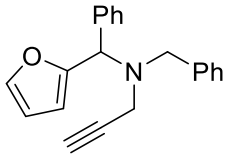
^{19}F NMR (377 MHz, $CDCl_3$) δ -112.13. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{27}H_{23}NOF$ 396.1752, found 396.1758.

1-(4-Bromophenyl)-3-ethylidene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4t)



By following the general procedure, the reaction was performed with furan-2-yl(phenyl)methanol **1a** (0.100 g, 0.57 mol) and 4-bromo-*N*-(but-2-yn-1-yl)aniline **2p** (0.127 g, 0.57 mol) in 1,4-dioxane (2 ml, 0.3m) were added $B(C_6F_5)_3$ (0.029 g, 10 mol%) and allowed to stir at 60 °C until complete conversion of starting material (by TLC analysis). To reaction mixture triethylamine (16 µl, 0.2 equiv), $Cu(OTf)_2$ (10 mg, 0.05 equiv) and TPP (30 mg, 0.2 equiv) were added sequentially. The reaction was allowed to stir at 90 °C until completion of reaction. After completion of reaction, reaction mixture was filtered and crude residue was purified by silica gel column chromatography (10% EtOAc/hexanes) to afford **4t** (0.088 g, 41%) as off-white semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 5.9, 1.8 Hz, 1H), 7.37 – 7.27 (m, 7H), 6.60 – 6.52 (m, 2H), 6.42 (dd, *J* = 5.9, 1.8 Hz, 1H), 5.89 (dt, *J* = 7.3, 1.9 Hz, 1H), 4.98 (s, 1H), 4.37 – 4.23 (m, 1H), 3.90 (d, *J* = 13.1 Hz, 1H), 1.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.4, 155.8, 144.8, 140.4, 136.0, 135.2, 132.4, 128.8, 127.4, 127.2, 125.4, 115.0, 110.0, 76.3, 64.8, 53.5, 15.0. IR (thin film) ν_{max} (cm^{-1}) 3130, 3115, 3093, 3004, 2912, 2824, 1732, 1595, 1558, 1489, 1371, 1246, 1127, 779, 369. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{21}H_{19}NOBr$ 380.0650, found 380.0636.

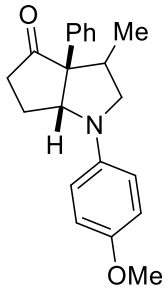
***N*-Benzyl-*N*-(furan-2-yl(phenyl)methyl)prop-2-yn-1-amine (4u′)**



The reaction was performed with furan-2-yl(phenyl)methanol **1a** (0.100 g, 0.57 mol) and *N*-benzylprop-2-yn-1-amine **2q** (0.082 g, 0.57 mol) in 1,4-dioxane (2 ml, 0.3 m) were added $B(C_6F_5)_3$ (0.029 g, 10 mol%) and allowed to stir at 60 °C until complete conversion of starting material (by TLC analysis) After completion of reaction, reaction mixture was filtered and crude residue was purified by silica gel column chromatography (10% EtOAc/hexanes) to afford **4u′** (0.108 g, 63%) as white solid. mp 74-75 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (dd, J = 5.2, 3.4 Hz, 2H), 7.34 (dddd, J = 11.4, 8.2, 7.5, 1.3 Hz, 8H), 7.23 (s, 1H), 6.33 (ddd, J = 5.0, 3.2, 1.3 Hz, 2H), 4.95 (s, 1H), 3.62 (q, J = 13.3 Hz, 2H), 3.28 – 3.04 (m, 2H), 2.26 (t, J = 2.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 142.4, 140.1, 139.1, 129.0, 128.6, 128.4, 127.7, 127.2, 78.8, 73.5, 64.2, 54.4, 39.3. HRMS (ESI) m/z calculated for [M+H]+ $C_{21}H_{20}NO$ 302.1545, found 302.1554.

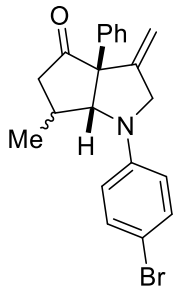
2.5. Product Derivatization

1-(4-Methoxyphenyl)-3-methyl-1,3a-diphenylhexahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (5)



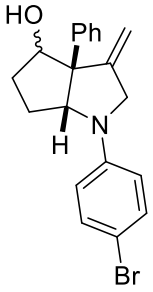
To a flask charged with a solution of compound **4c** (50 mg, 0.157 mmol) in EtOAc (1 mL) was added Pd/C (4 mg, 10 wt%) in one portion. The flask was evacuated and refilled with H_2 with a balloon.[3a] The reaction mixture was stirred under H_2 atmosphere for 2 h before it was filtered through a pad of celite, which was washed with EtOAc (2 mL x 3). The filtrate was concentrated, and the crude mixture was purified by silica gel column chromatography to give product **5** (0.035 g, 69%) as pale yellow solid. mp 120-121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.30 (m, 5H), 6.89 (d, J = 9.0 Hz, 2H), 6.62 (d, J = 9.0 Hz, 2H), 4.63 (d, J = 3.7 Hz, 1H), 3.78 (s, 3H), 3.65 – 3.54 (m, 1H), 3.27 – 3.12 (m, 1H), 2.69 – 2.57 (m, 1H), 2.34 (t, J = 4.3 Hz, 3H), 2.03 – 1.88 (m, 1H), 1.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 219.0, 151.4, 140.9, 137.7, 128.8, 127.2, 127.0, 114.9, 113.7, 68.8, 66.1, 57.3, 55.9, 43.5, 38.0, 22.8, 11.5. IR (thin film) ν_{max} (cm^{-1}) 3099, 3021, 2932, 2915, 2840, 1791, 1508, 1487, 1237, 1200, 1129, 783, 588. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{21}H_{24}NO_2$ 322.1807, found 322.1805.

1-(4-Bromocyclohexa-1,5-dien-1-yl)-6-methyl-3-methylene-3a-phenylhexahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (6)



To a solution of **4f** (0.50 g, 0.14 mmol), MeMgBr (0.09 mL g, 0.27 mmol) was added in Et_2O (2 mL) at 0 °C and stirred for 30 min at rt. The reaction was quenched with aq. NH_4Cl solution and the mixture stirred for 5 min. The resulting mixture was extracted with Et_2O (3 × 2 mL). The combined extracts were dried ($MgSO_4$), filtered and concentrated to afford **6** (0.043 g, 84%) as off-white semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) (*dr* 5:1) δ (for major diastereomer) 7.43 – 7.25 (m, 7H), 6.53 (d, *J* = 8.8 Hz, 2H), 5.35 (s, 1H), 5.20 (s, 1H), 4.44 (d, *J* = 5.0 Hz, 1H), 4.13 (dd, *J* = 43.7, 13.8 Hz, 2H), 2.78 (dd, *J* = 18.0, 7.9 Hz, 1H), 2.43 – 2.34 (m, 1H), 2.20 (dd, *J* = 18.0, 7.7 Hz, 1H), 1.22 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (minor diastereomer peak in parenthesis) 212.7, 146.3 (146.0), 145.5 (144.8), 139.7 (132.2), 132.1 (128.8), 128.7, 127.4 (126.4), 127.0 (125.9), 114.0 (113.0), 111.7 (110.5), 108.8 (108.5), 75.8 (72.2), 68.2 (64.4), (54.5) 53.7, (47.3) 45.7, 34.0 (31.3), 19.9 (16.4). IR (thin film) ν_{max} (cm^{-1}) 3391, 3096, 1797, 1607, 1494, 1477, 1378, 1251, 1124, 1084, 893, 785, 568. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{21}H_{21}NOBr$ 382.0807, found 382.0818.

1-(4-Bromophenyl)-3-methylene-3a-phenyloctahydrocyclopenta[*b*]pyrrol-4-ol (7)

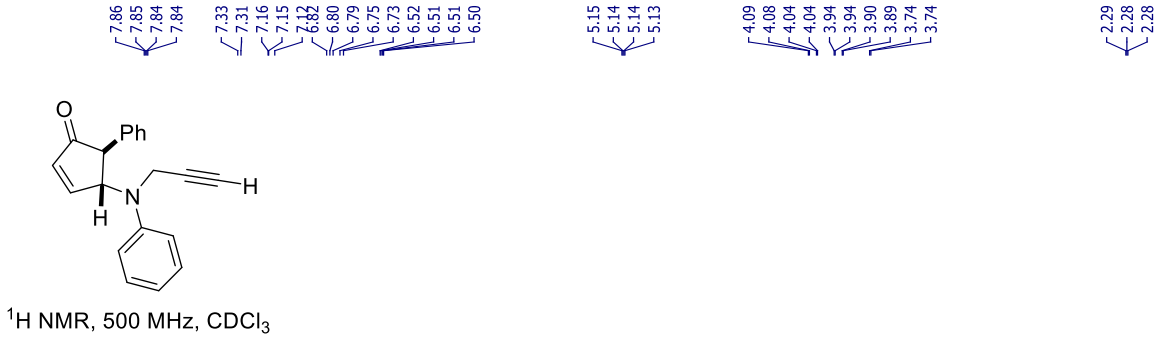


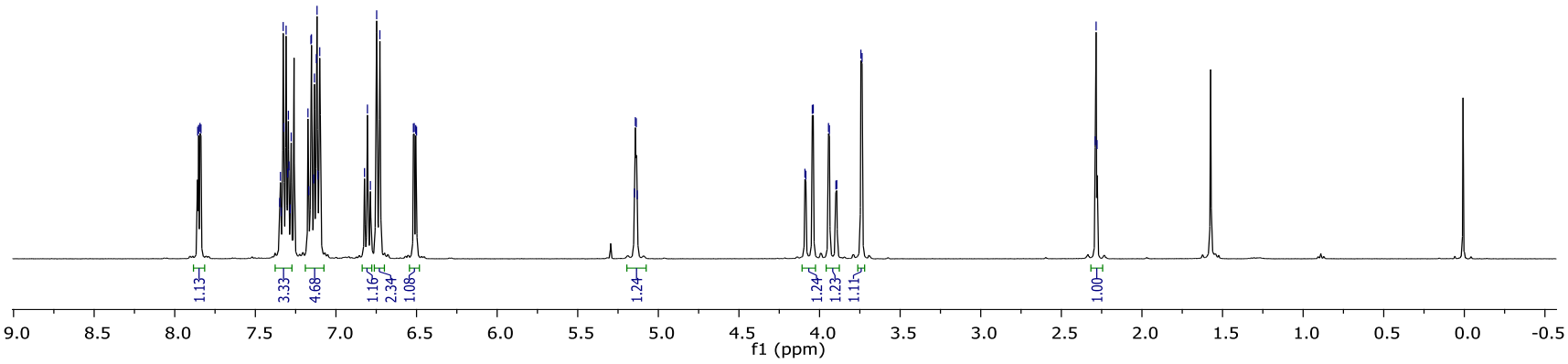
To a solution of **4f** (0.50 g, 0.15 mmol), $NaBH_4$ (0.011 g, 0.29 mmol) was added in MeOH (0.5 mL) at 0 °C and stirred for 30 min at rt.[3b] The reaction was quenched with H_2O (0.5 mL) and

themixture stirred for 5 min. The resulting mixture was extracted with Et_2O (2 × 2 mL). The combined extracts were dried ($MgSO_4$), filtered and concentrated to afford **7** (0.040 g, 80%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) (*dr* >6:1) δ (for major diastereomer) 7.53 (d, *J* = 6.6 Hz, 2H), 7.38 (dd, *J* = 18.3, 7.5 Hz, 5H), 6.53 (d, *J* = 7.5 Hz, 2H), 5.43 (s, 1H), 4.93 (s, 1H), 4.61 (s, 2H), 4.36 (d, *J* = 13.8 Hz, 1H), 4.16 (d, *J* = 13.6 Hz, 1H), 2.23 – 2.10 (m, 2H), 1.93 – 1.78 (m, 2H), 1.55 – 1.47 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (minor diastereomer peak in parenthesis) 150.4 (148.8), 146.7 (145.3), 144.5 (137.7), (132.3) 132.1, (128.9) 128.6, (127.5) 126.6, 126.5 (126.2), (115.4) 114.7, (114.0) 112.5, (109.8) 108.8, (80.6) 77.6, (75.4) 71.9, (64.0) 62.8, 55.7 (52.9), 33.9, 26.2. IR (thin film) ν_{max} (cm^{-1}) 3310, 3095, 2862, 1560, 1490, 1380, 1245, 1139, 359, 333. HRMS (ESI) *m/z* calculated for $[M+H]^+$ $C_{20}H_{21}NOBr$ 370.0807, found 370.0814.

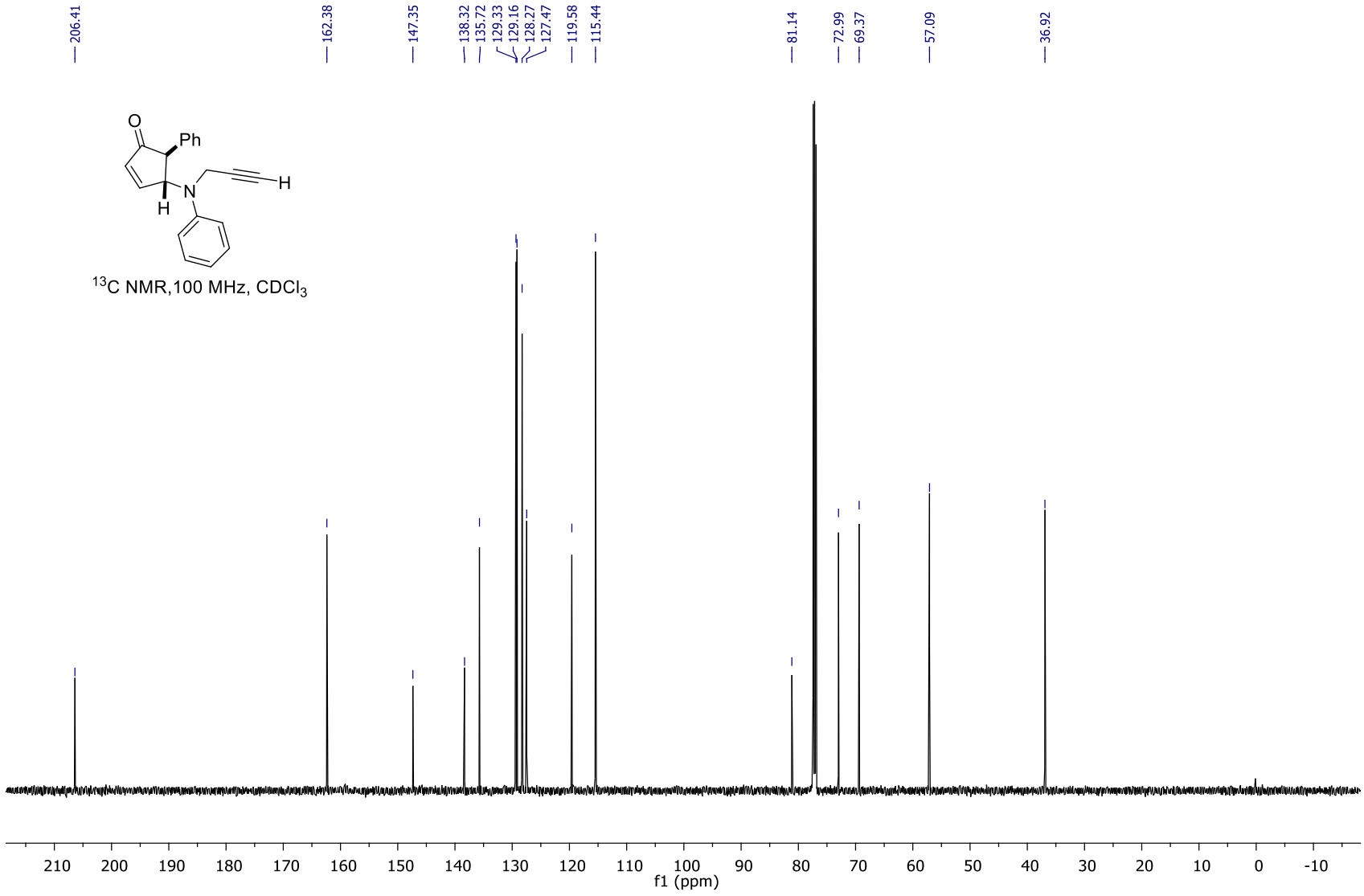
3. ^{1}H, ^{13}C and ^{19}F NMR Spectra of Compounds

4-(Ethynyl(phenyl)amino)-5-phenylcyclopent-2-en-1-one (3a)

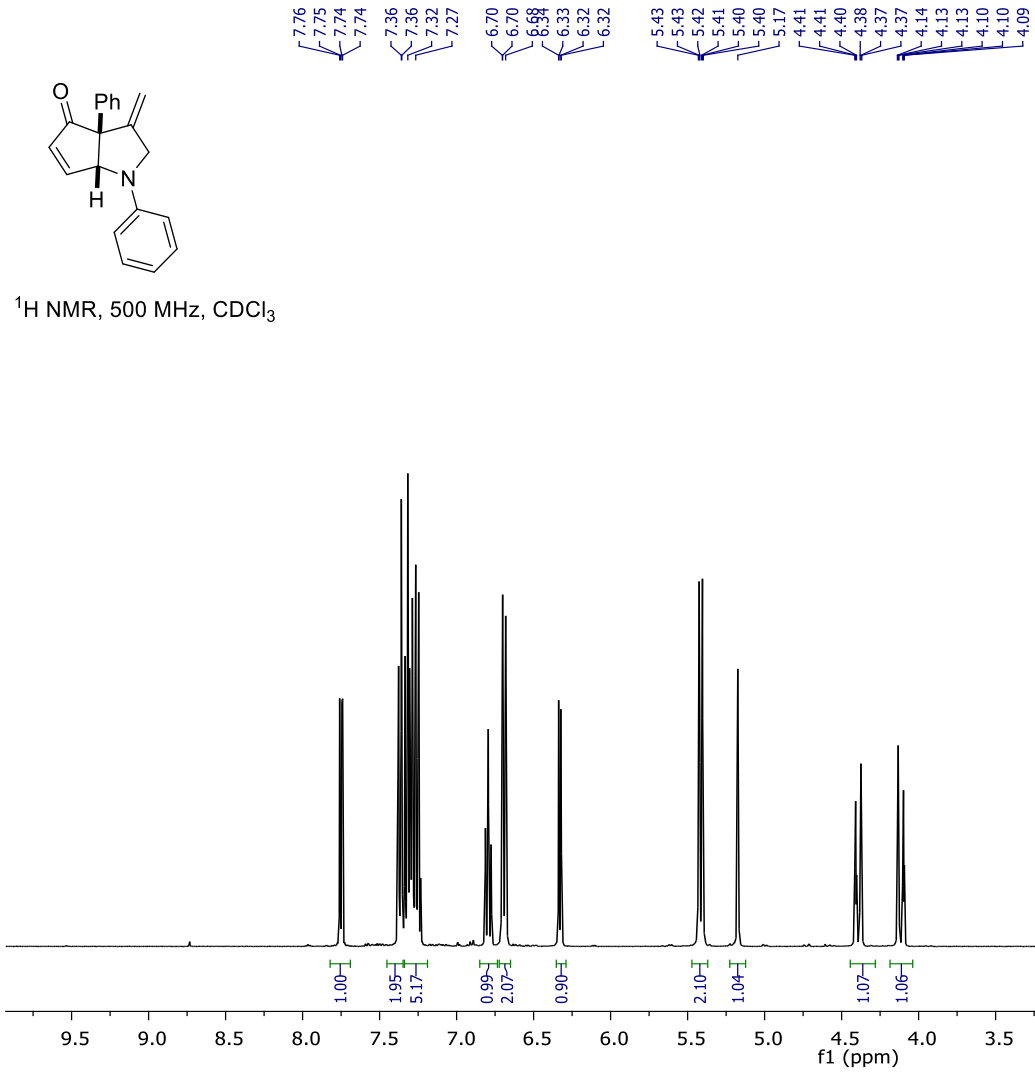




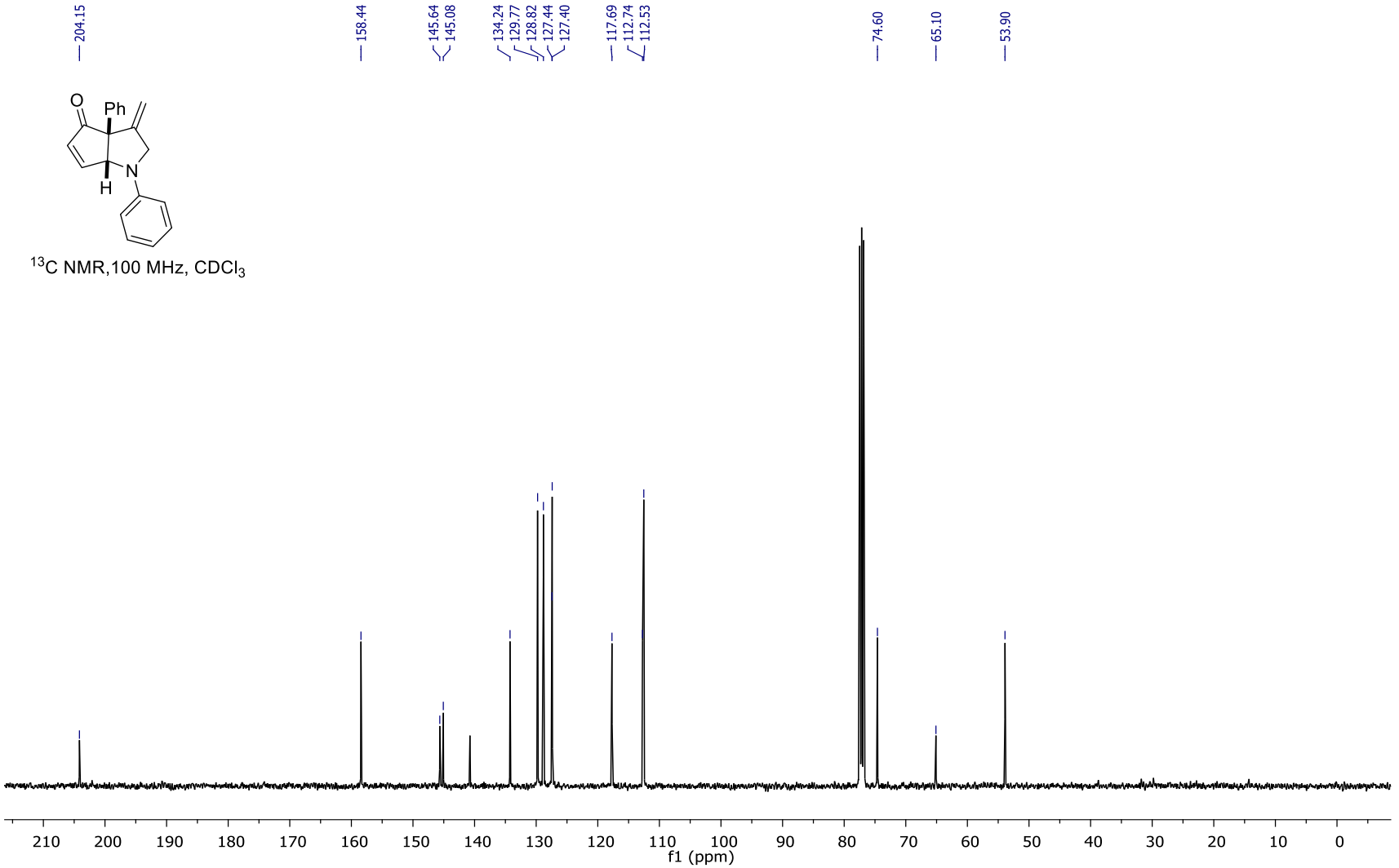
4-(Ethynyl(phenyl)amino)-5-phenylcyclopent-2-en-1-one (3a)



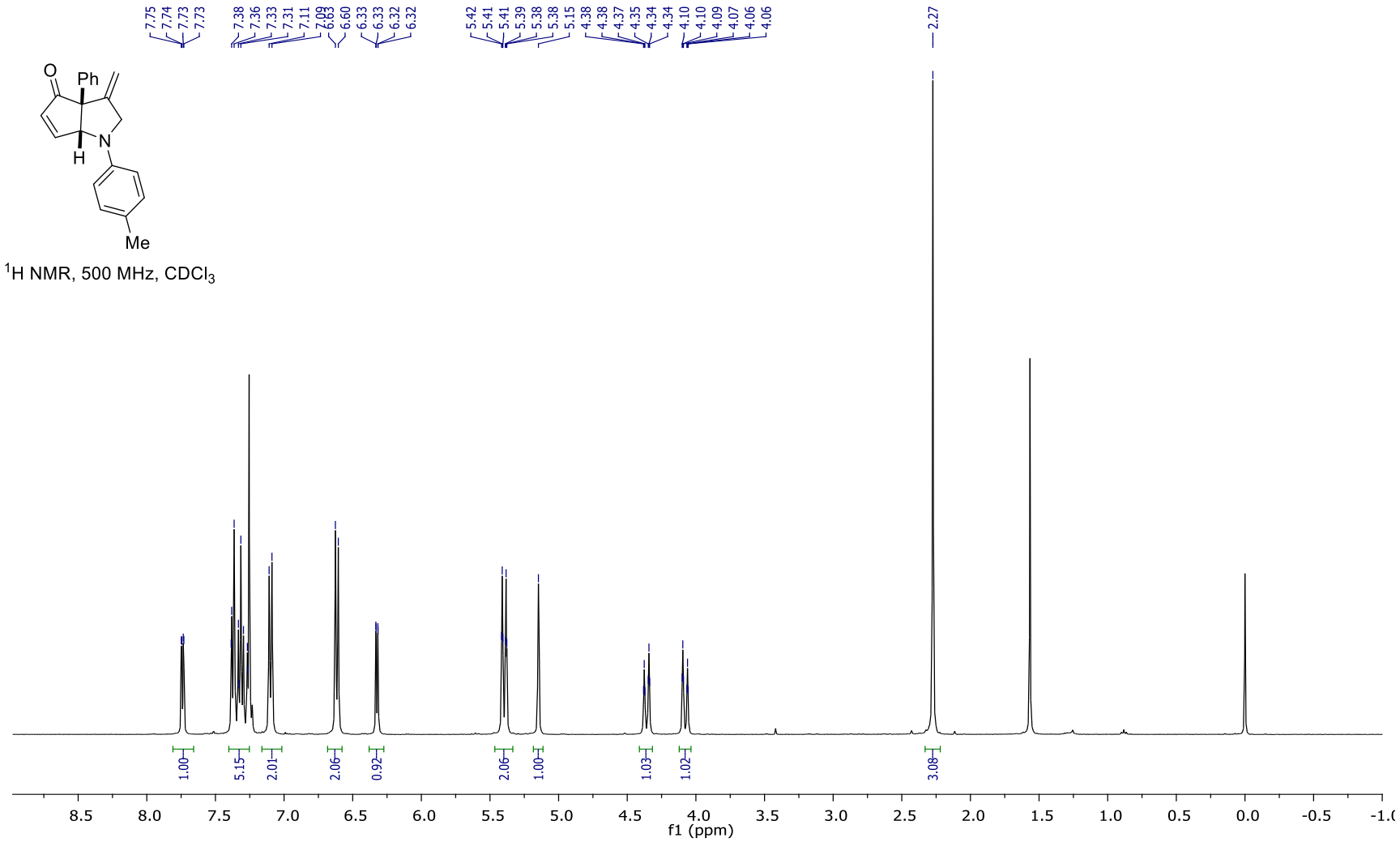
3-Methylene-1,3a-diphenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4a)



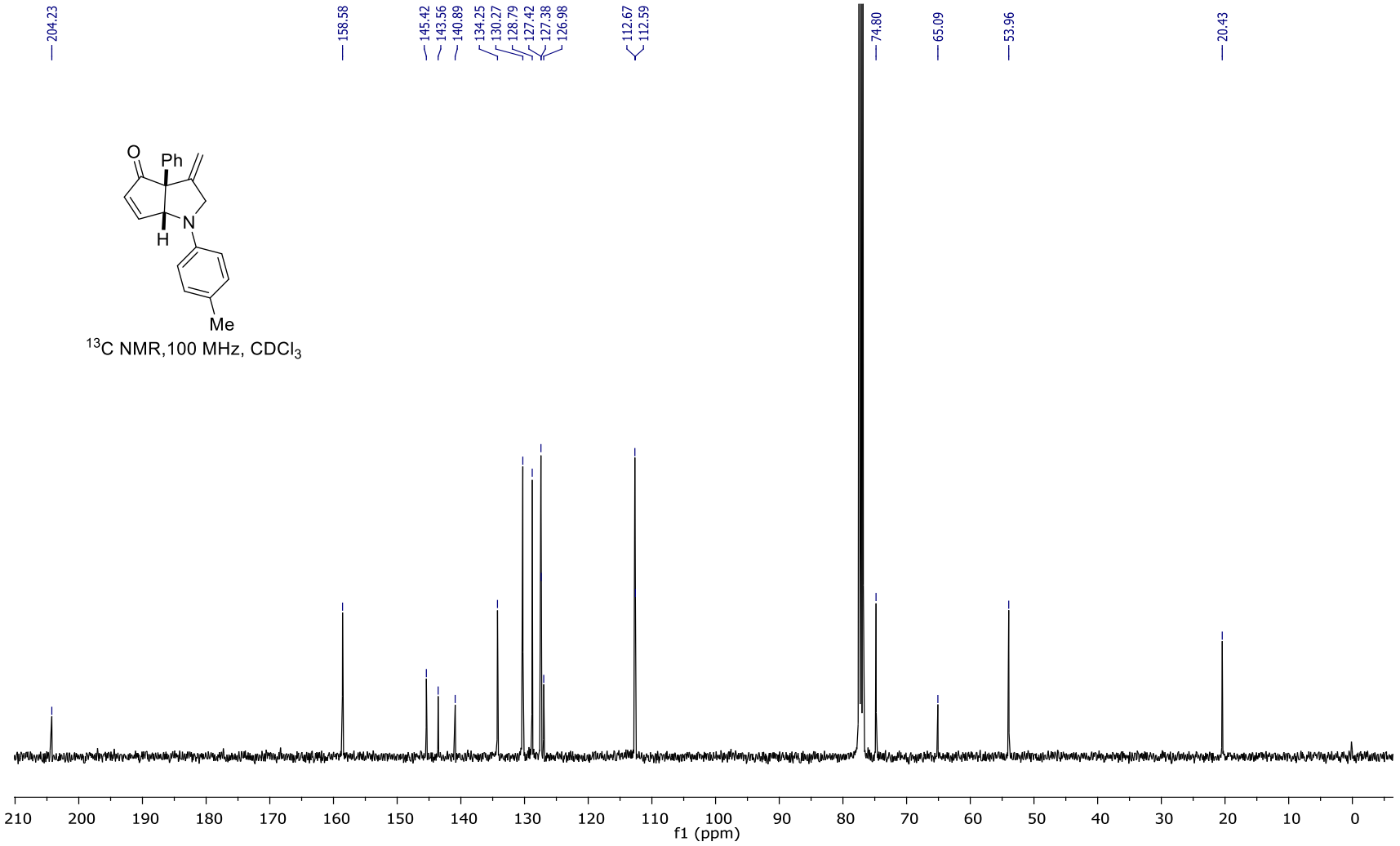
3-Methylene-1,3a-diphenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4a)



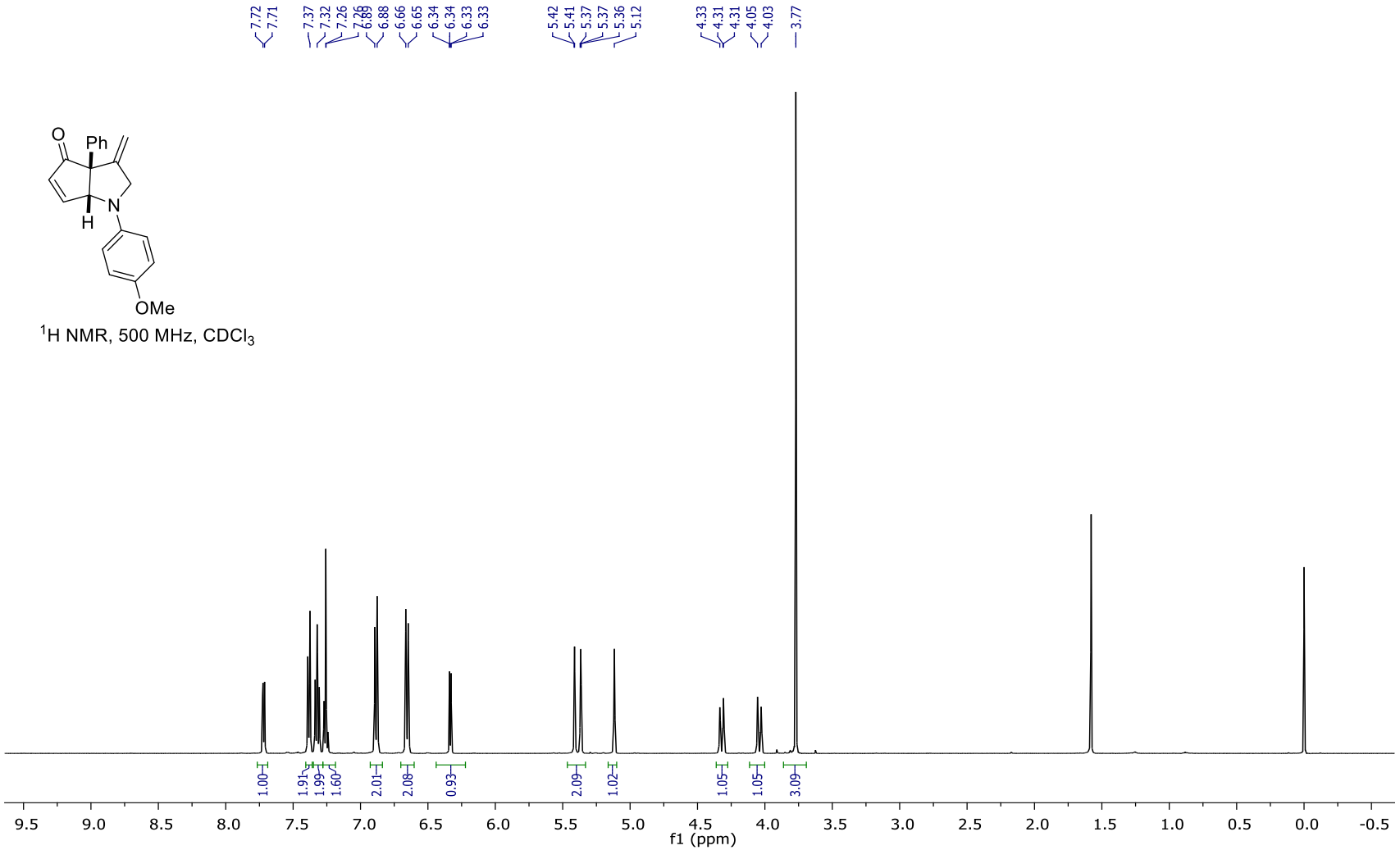
3-Methylene-3a-phenyl-1-(*p*-tolyl)-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4b)



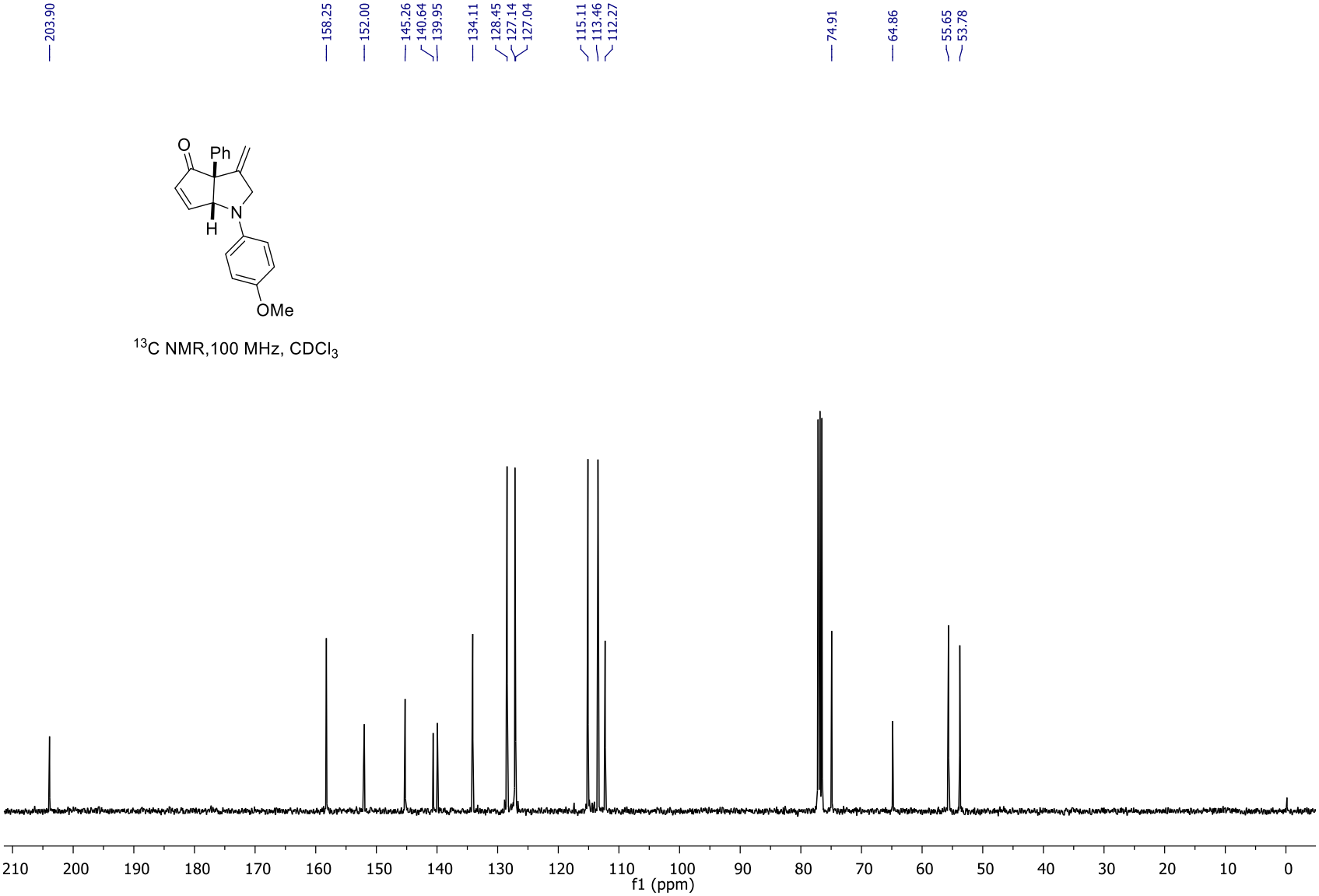
3-Methylene-3a-phenyl-1-(*p*-tolyl)-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4b)



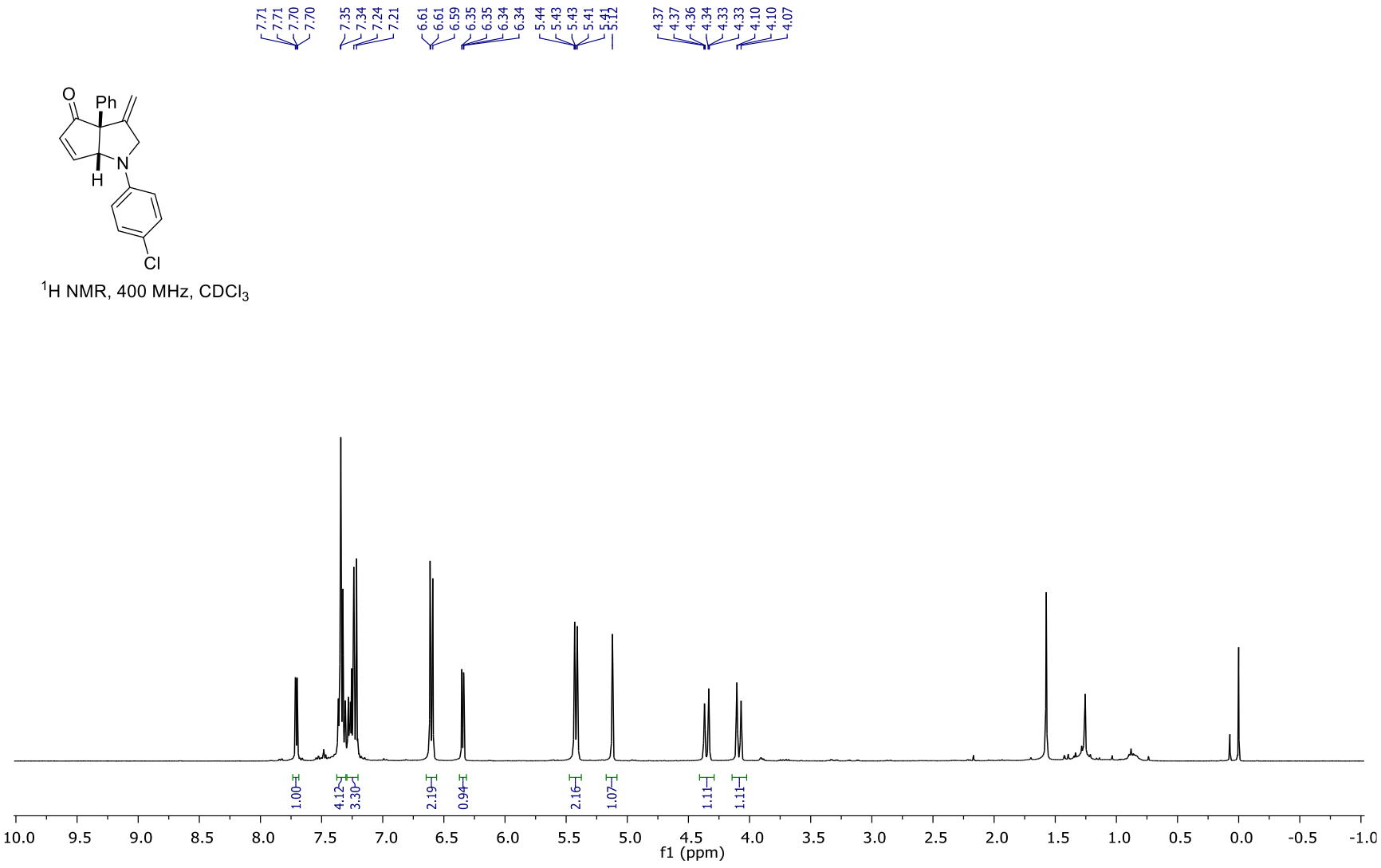
1-(4-Methoxyphenyl)-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4c)



1-(4-Methoxyphenyl)-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4c)

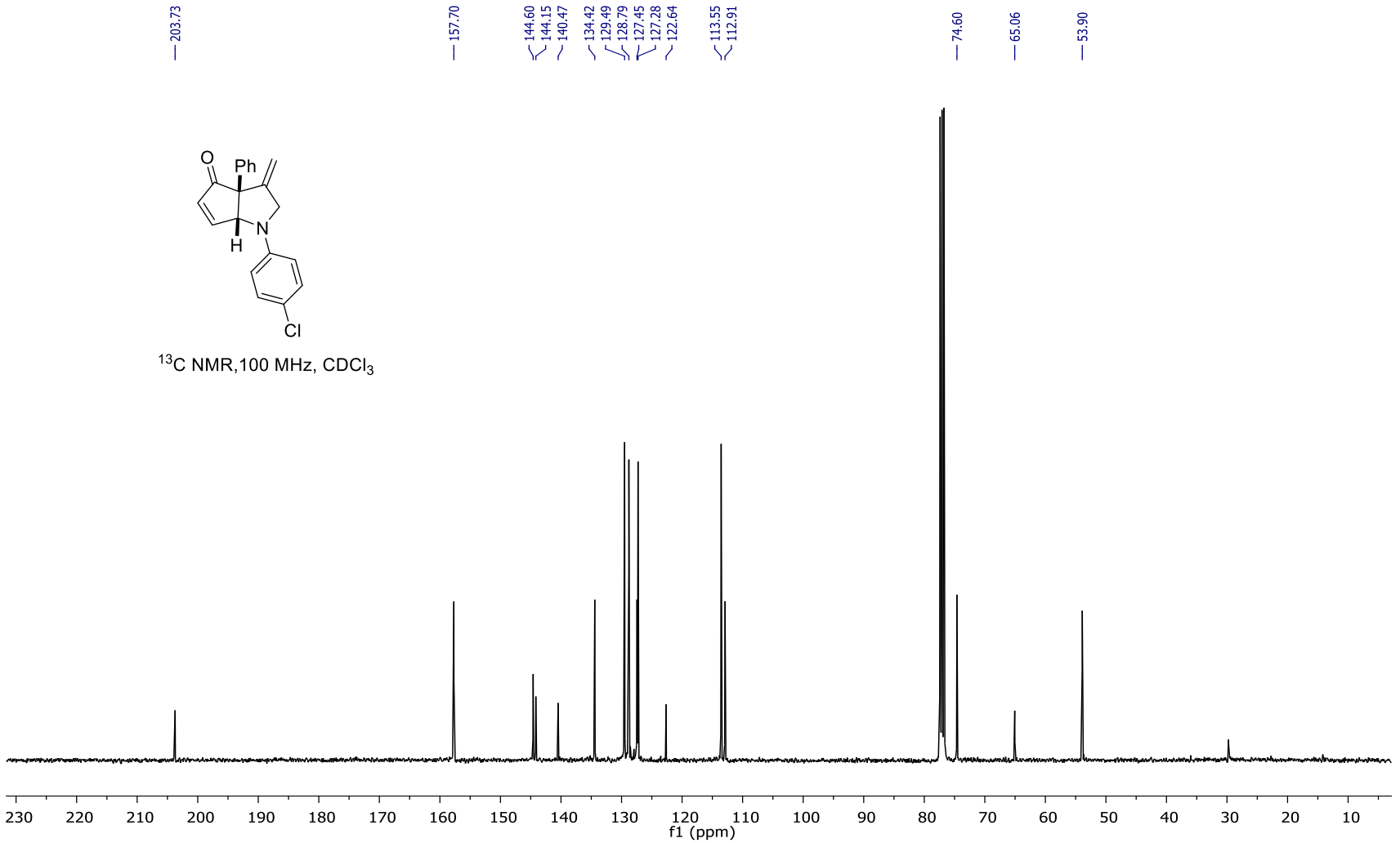


1-(4-Chlorophenyl)-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4d)

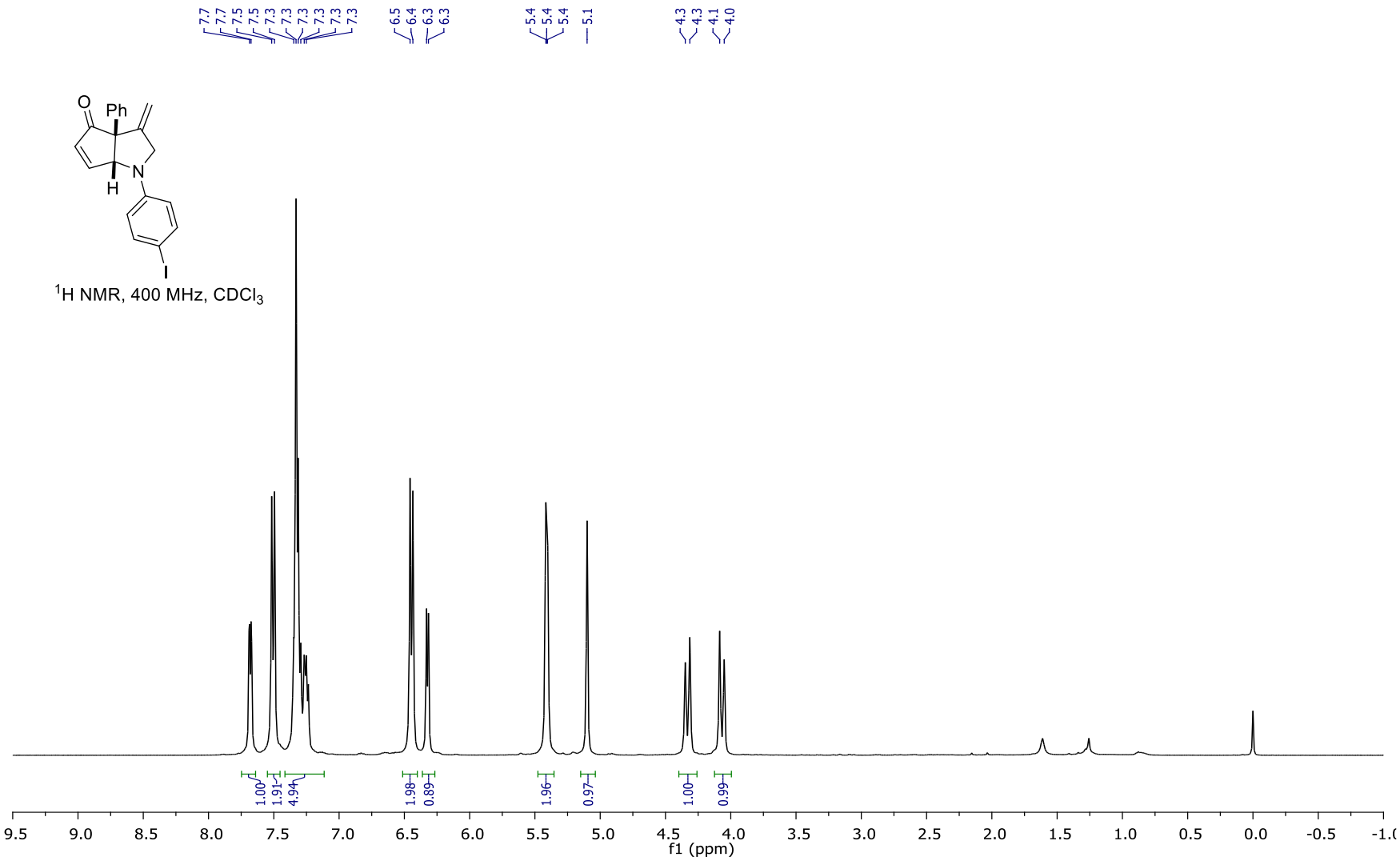


^{1}H NMR, 400 MHz, $CDCl_3$

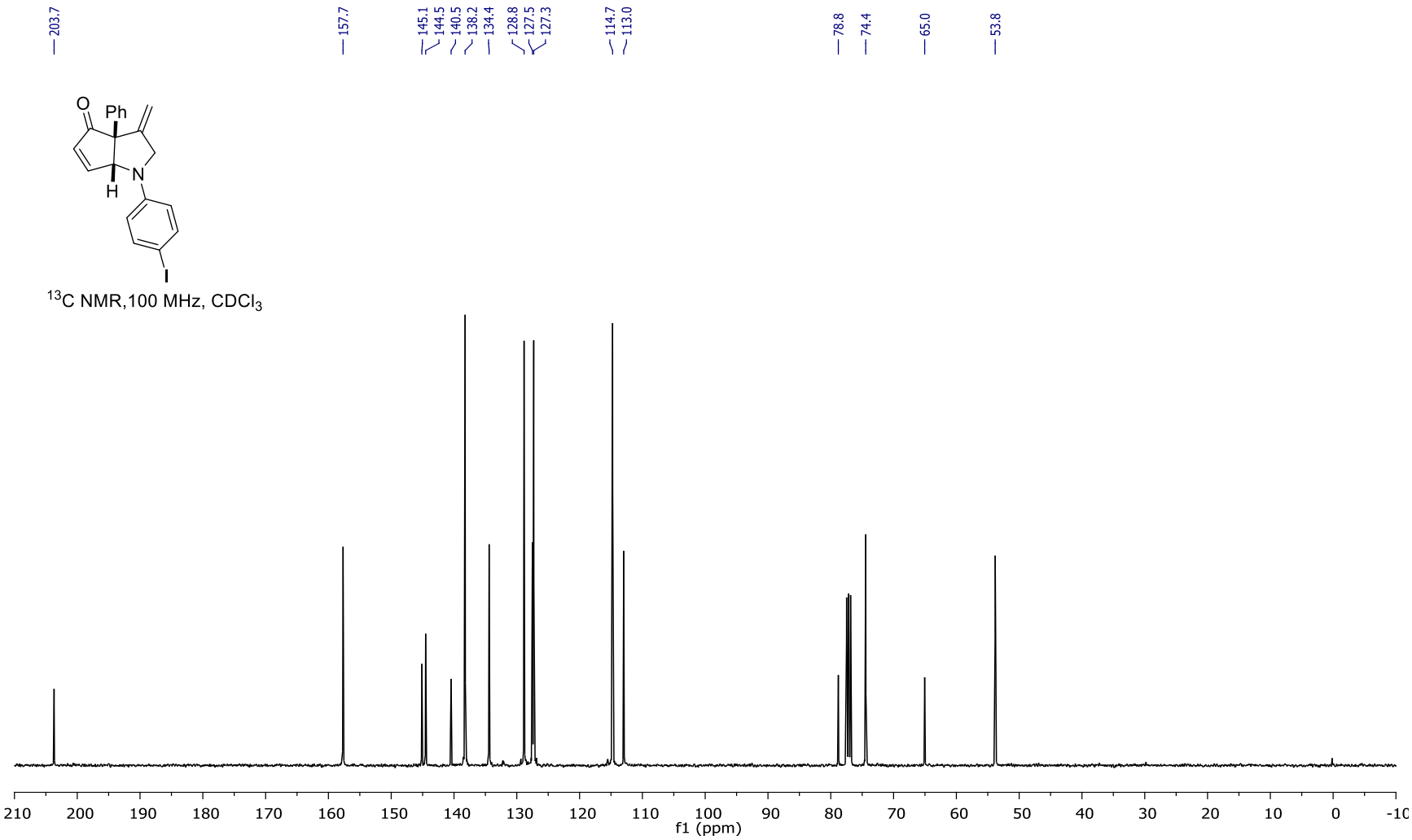
1-(4-Chlorophenyl)-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4d)



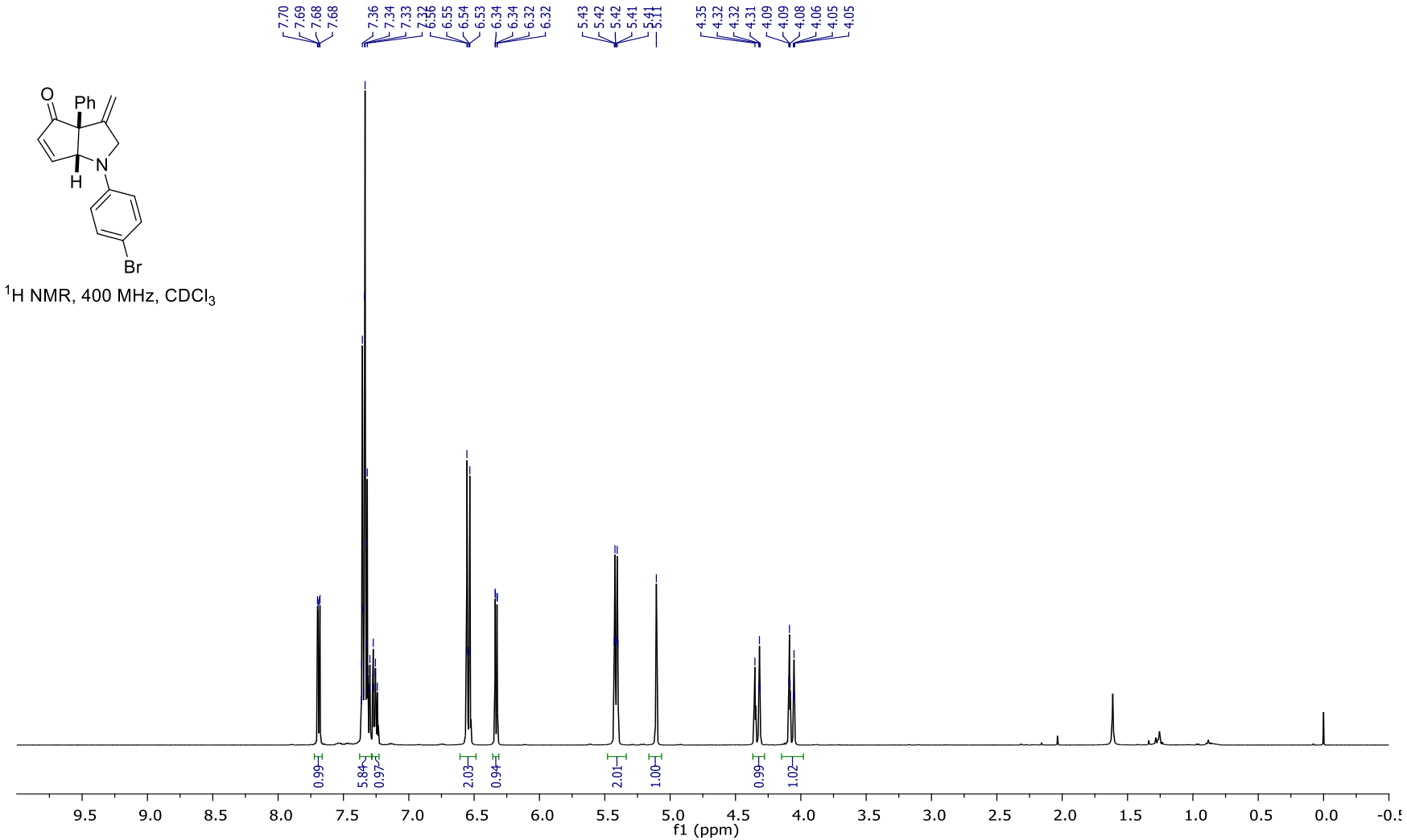
(4-Iodophenyl)-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4e)



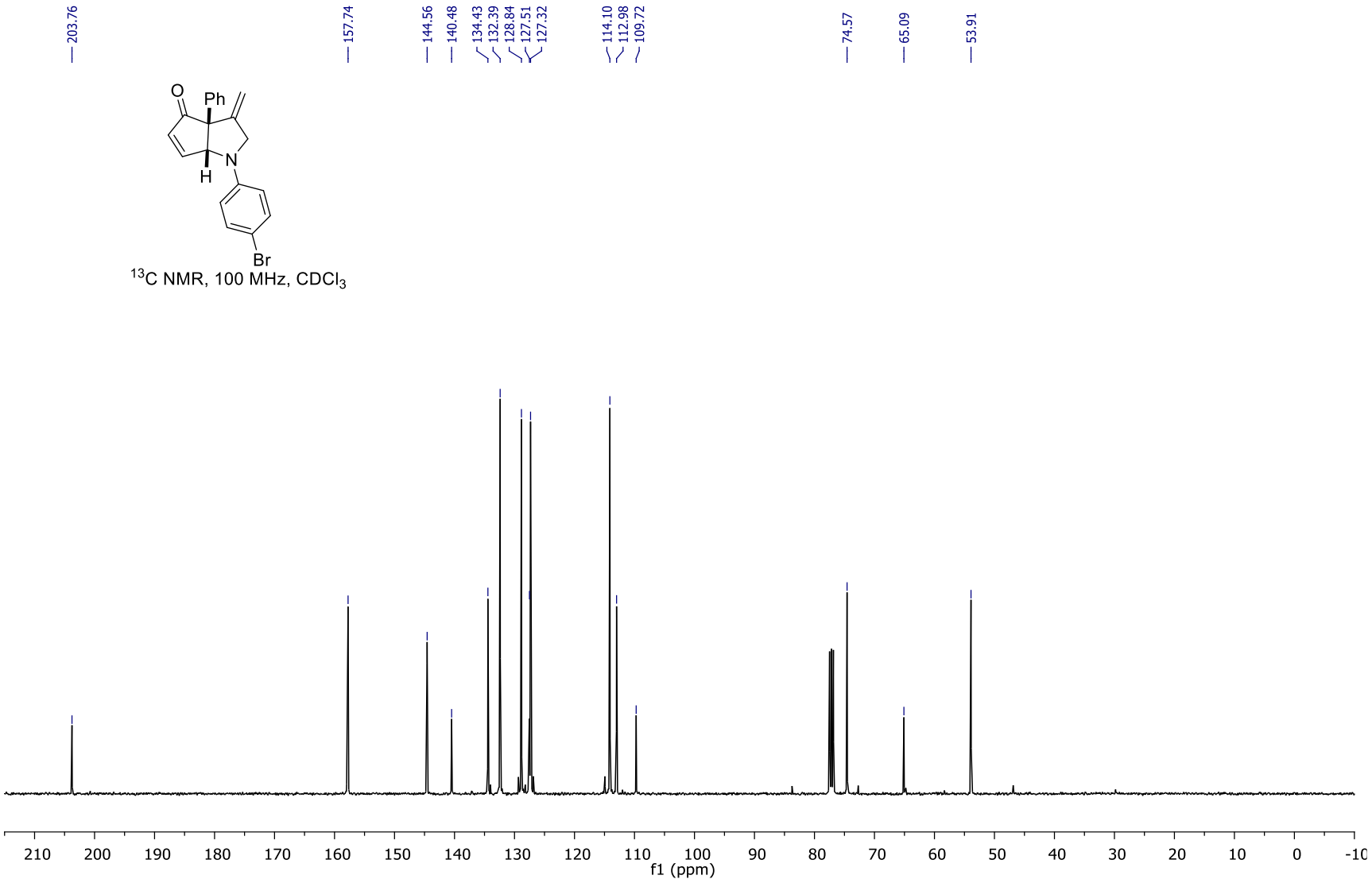
(4-Iodophenyl)-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4e)



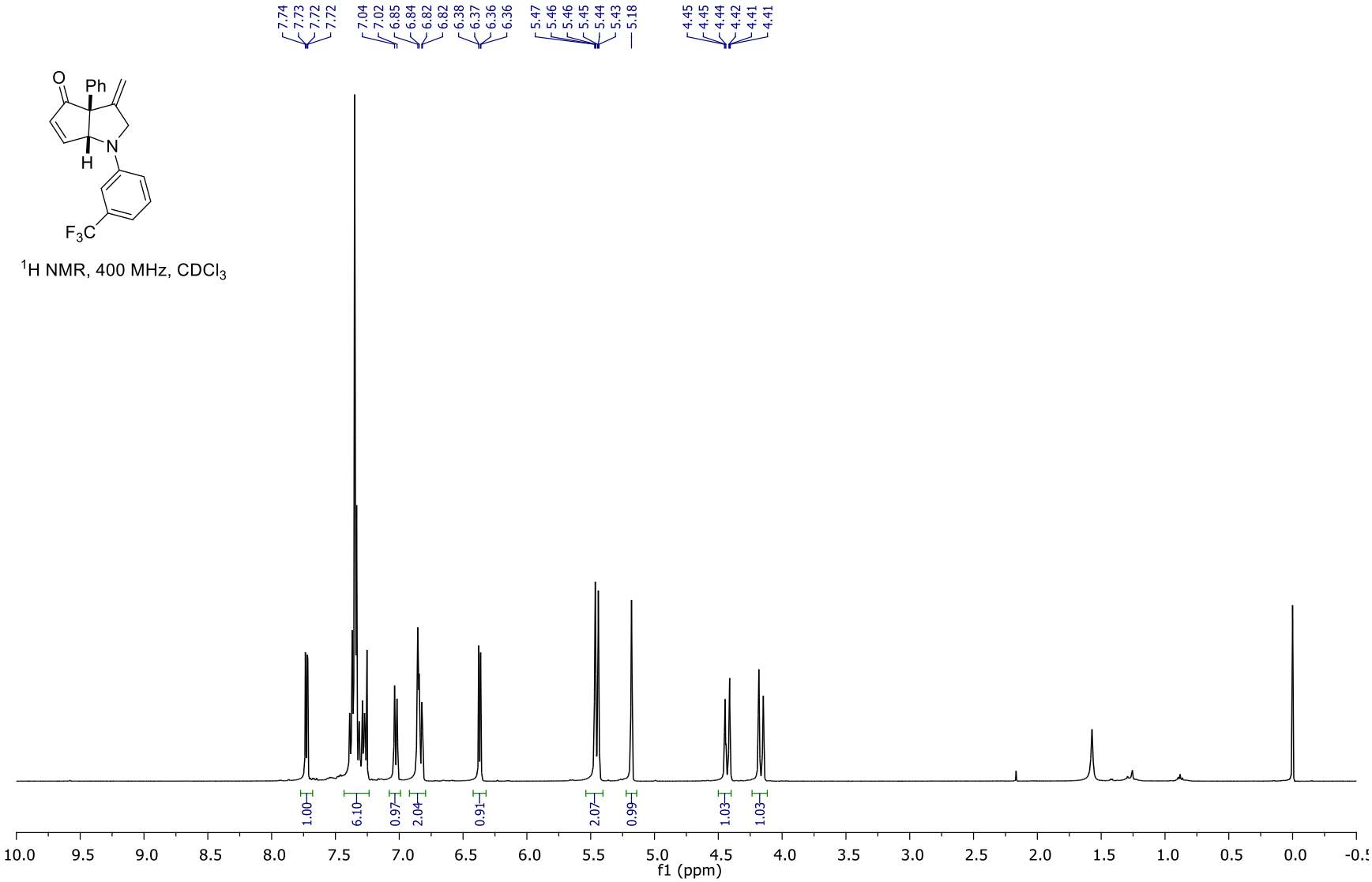
1-(4-Bromophenyl)-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*) -one (4f)



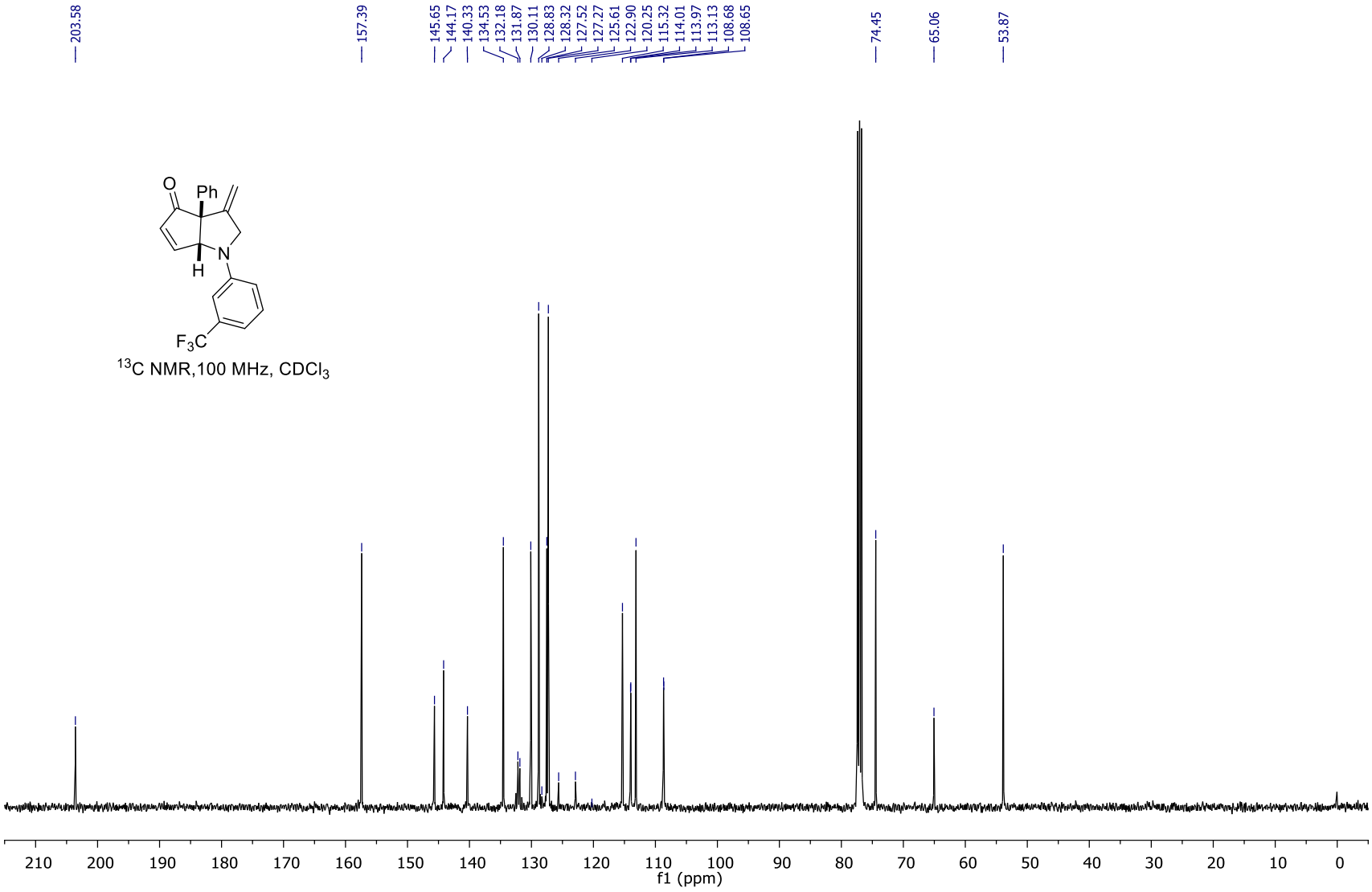
1-(4-Bromophenyl)-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*) -one (4f)



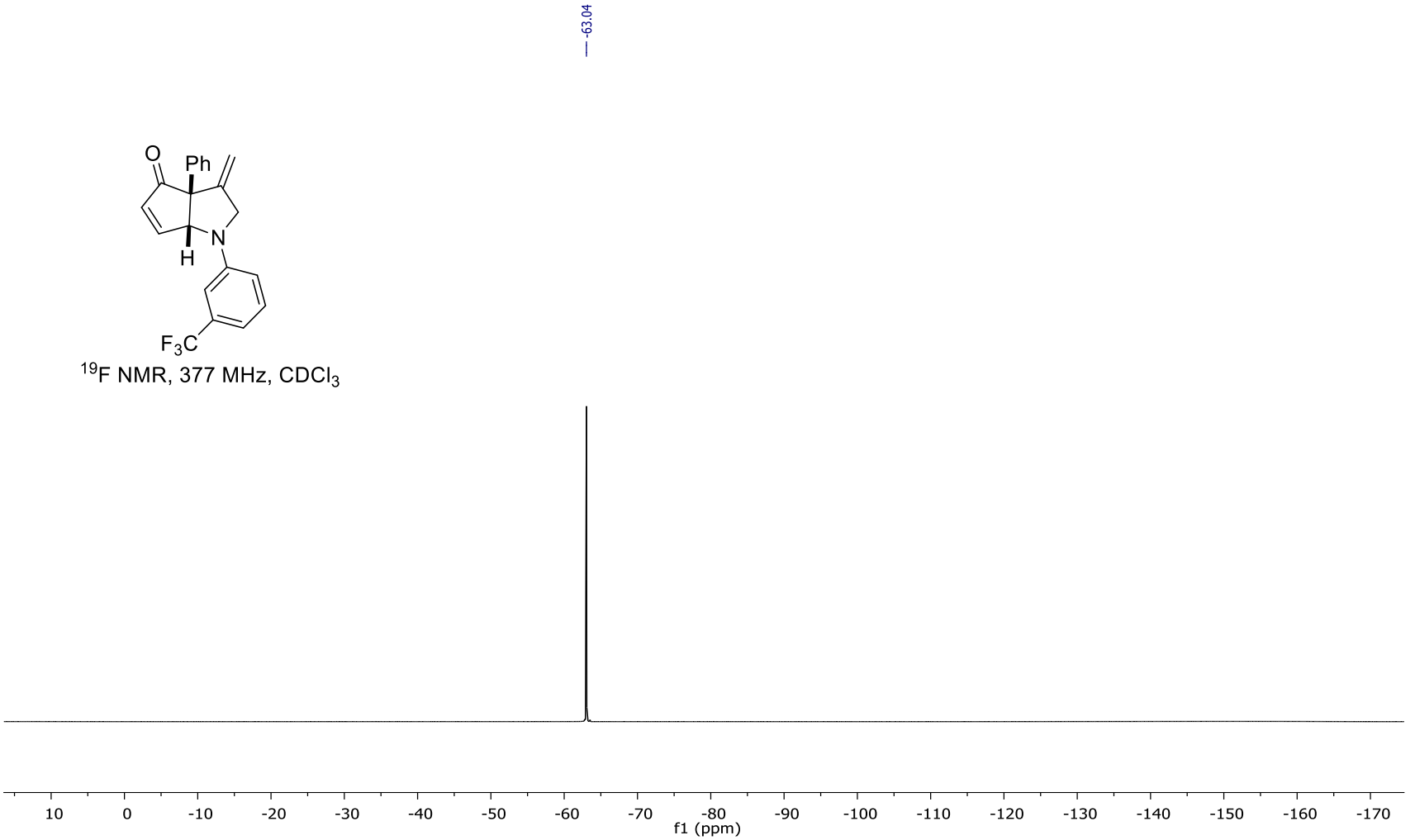
3-Methylene-3a-phenyl-1-(3-(trifluoromethyl)phenyl)-2,3,3a,6a-tetrahydrocyclopenta[*b*] pyrrol-4(1*H*)-one (4g)



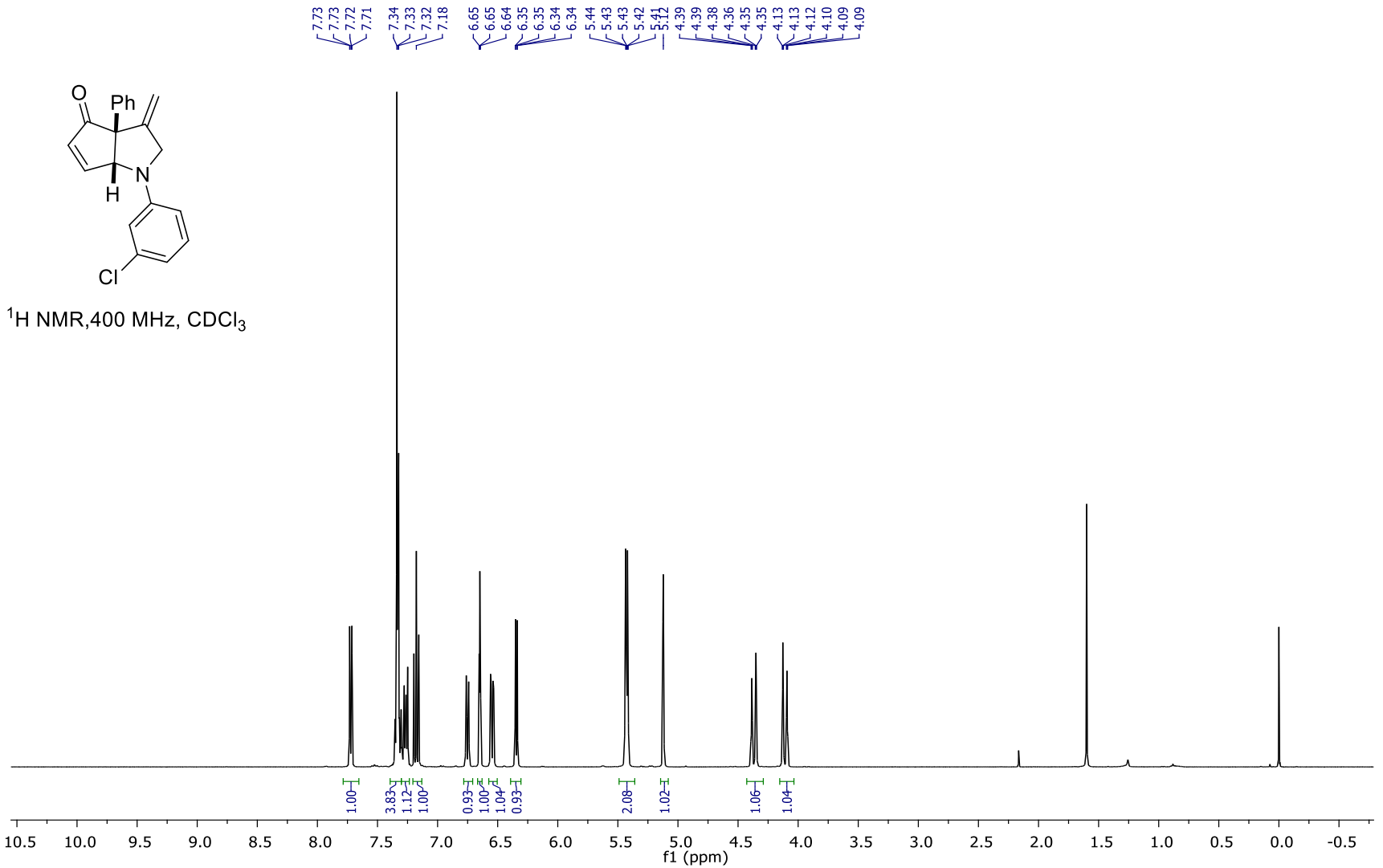
3-Methylene-3a-phenyl-1-(3-(trifluoromethyl)phenyl)-2,3,3a,6a-tetrahydrocyclopenta[*b*] pyrrol-4(1*H*)-one (4g)



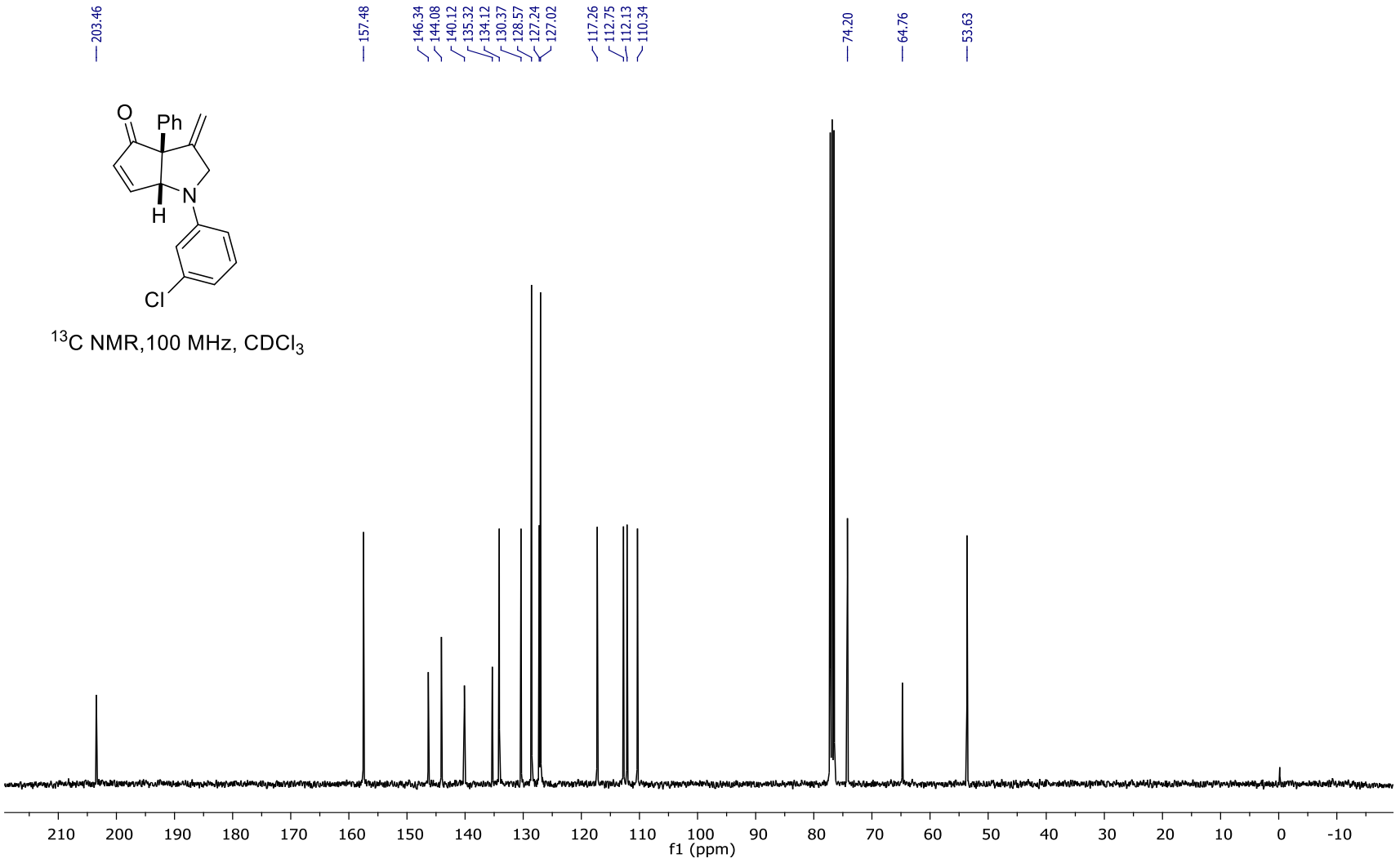
^{19}F 3-Methylene-3a-phenyl-1-(3-(trifluoromethyl)phenyl)-2,3,3a,6a-tetrahydrocyclopenta[*b*] pyrrol-4(1*H*)-one (4g)



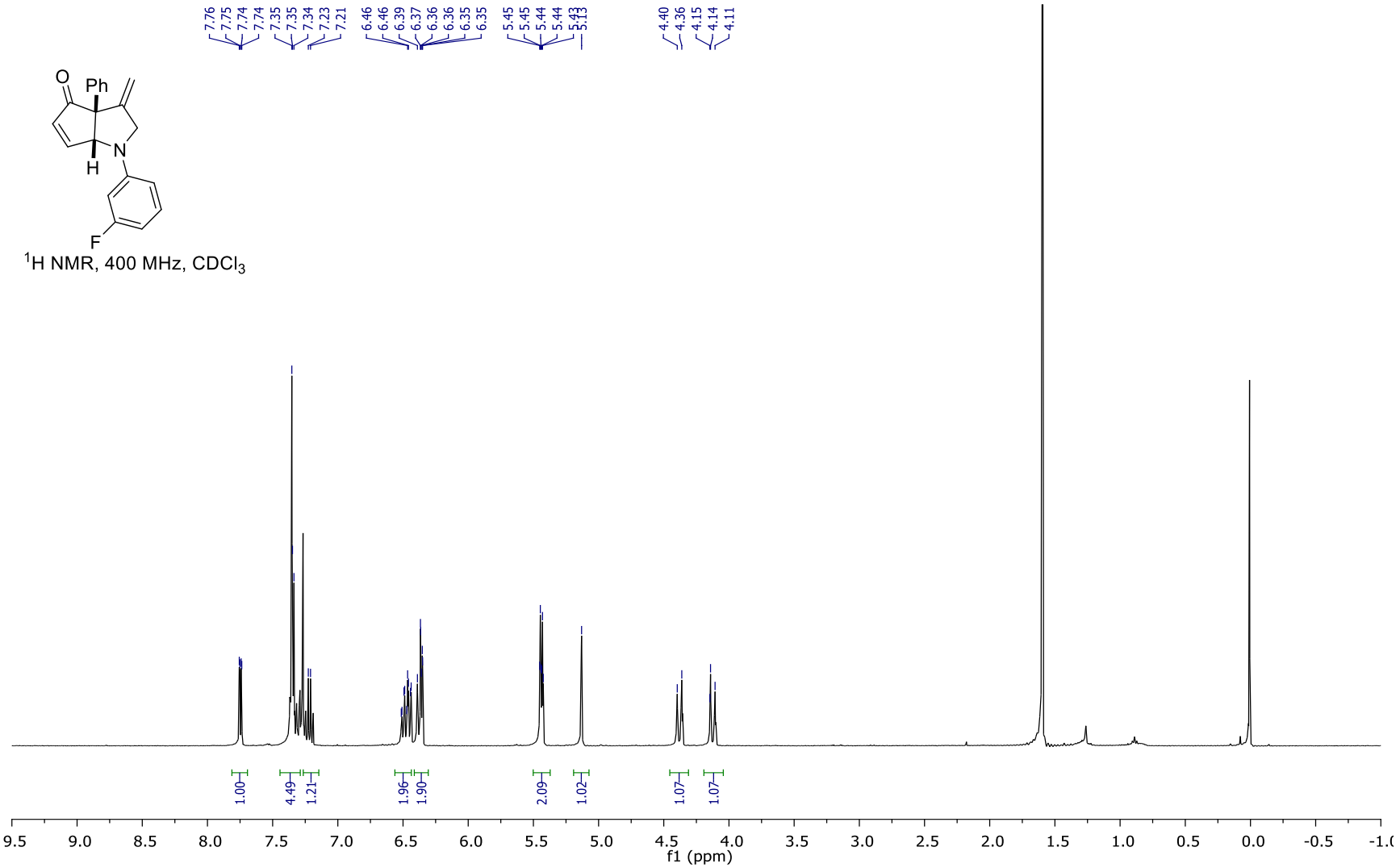
(3-Chlorophenyl)-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[b]pyrrol-4(1*H*)-one (4h)



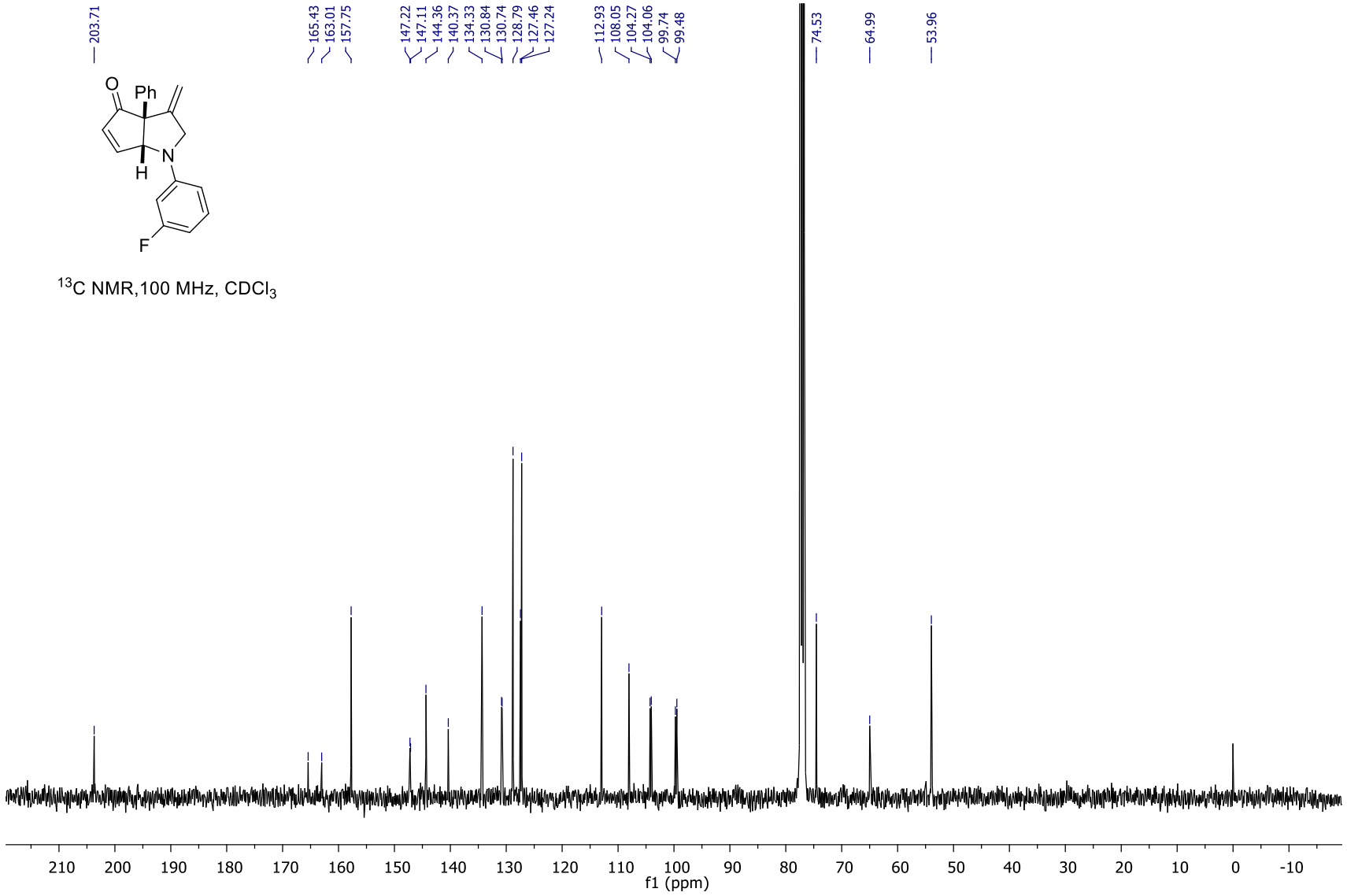
(3-Chlorophenyl)-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[b]pyrrol-4(1*H*)-one (4h)



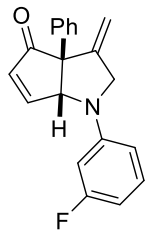
(3-Fluorophenyl)-6a-methyl-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4i)



(3-Fluorophenyl)-6a-methyl-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4i)

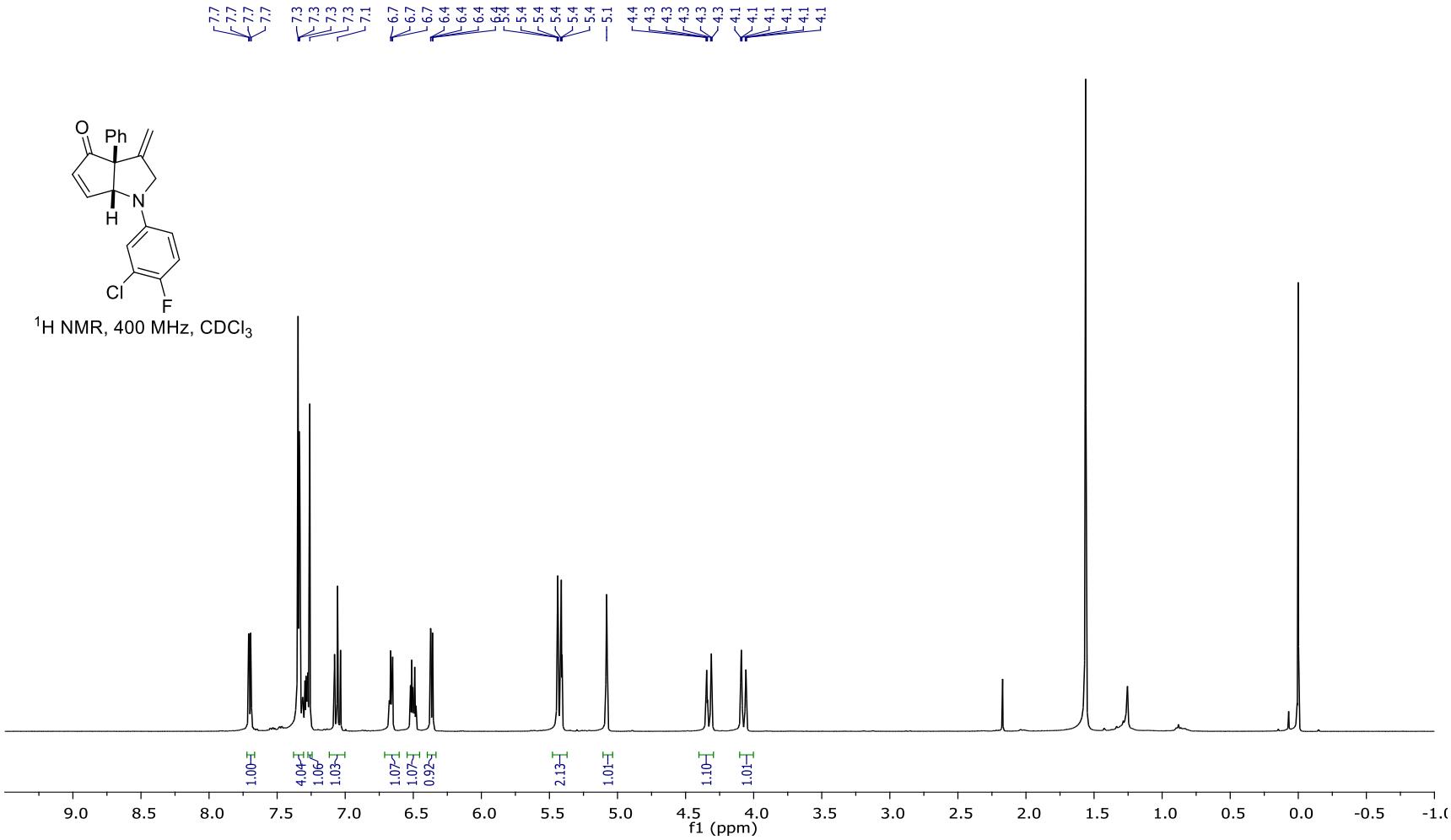


^{19}F Spectrum of (3-Fluorophenyl)-6a-methyl-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4i)

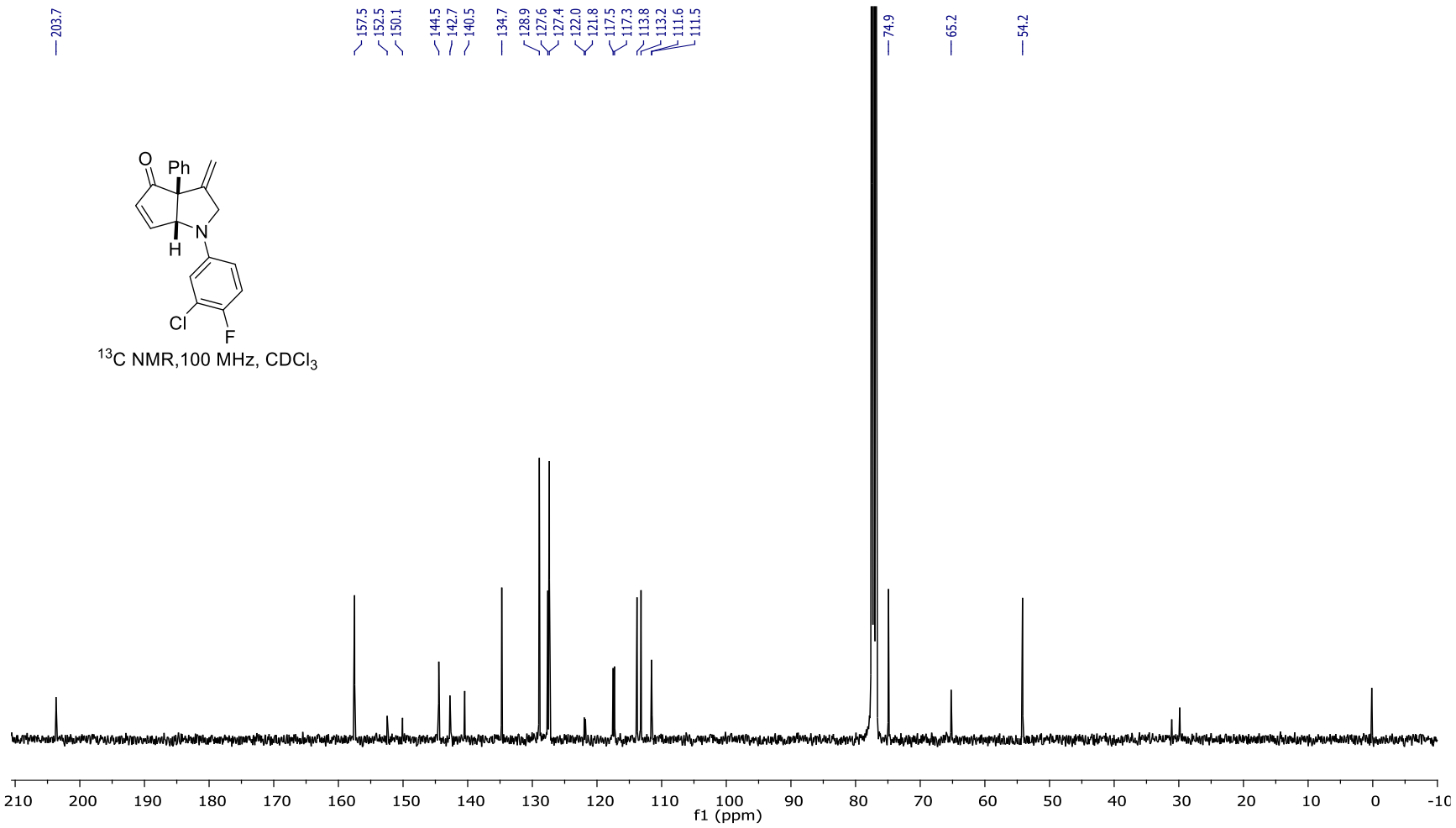


^{19}F NMR, 377 MHz, $CDCl_3$

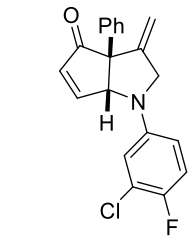
(3-Chloro-4-fluorophenyl)-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol -4(1*H*)-one (4j)



(3-Chloro-4-fluorophenyl)-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol -4(1*H*)-one (4j)

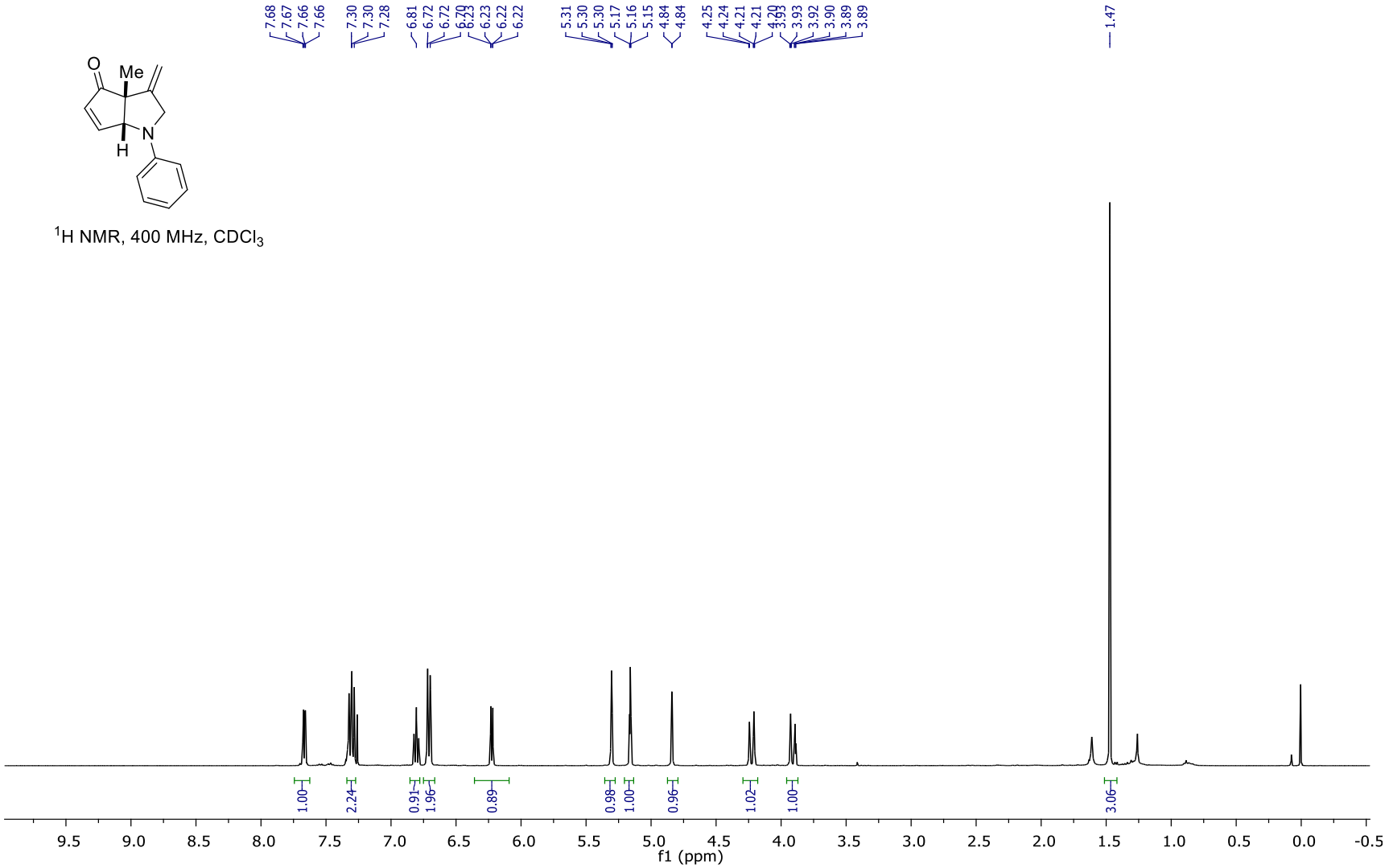


^{19}F Spectrum of (3-Chloro-4-fluorophenyl)-3-methylene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol -4(1*H*)-one (4j)

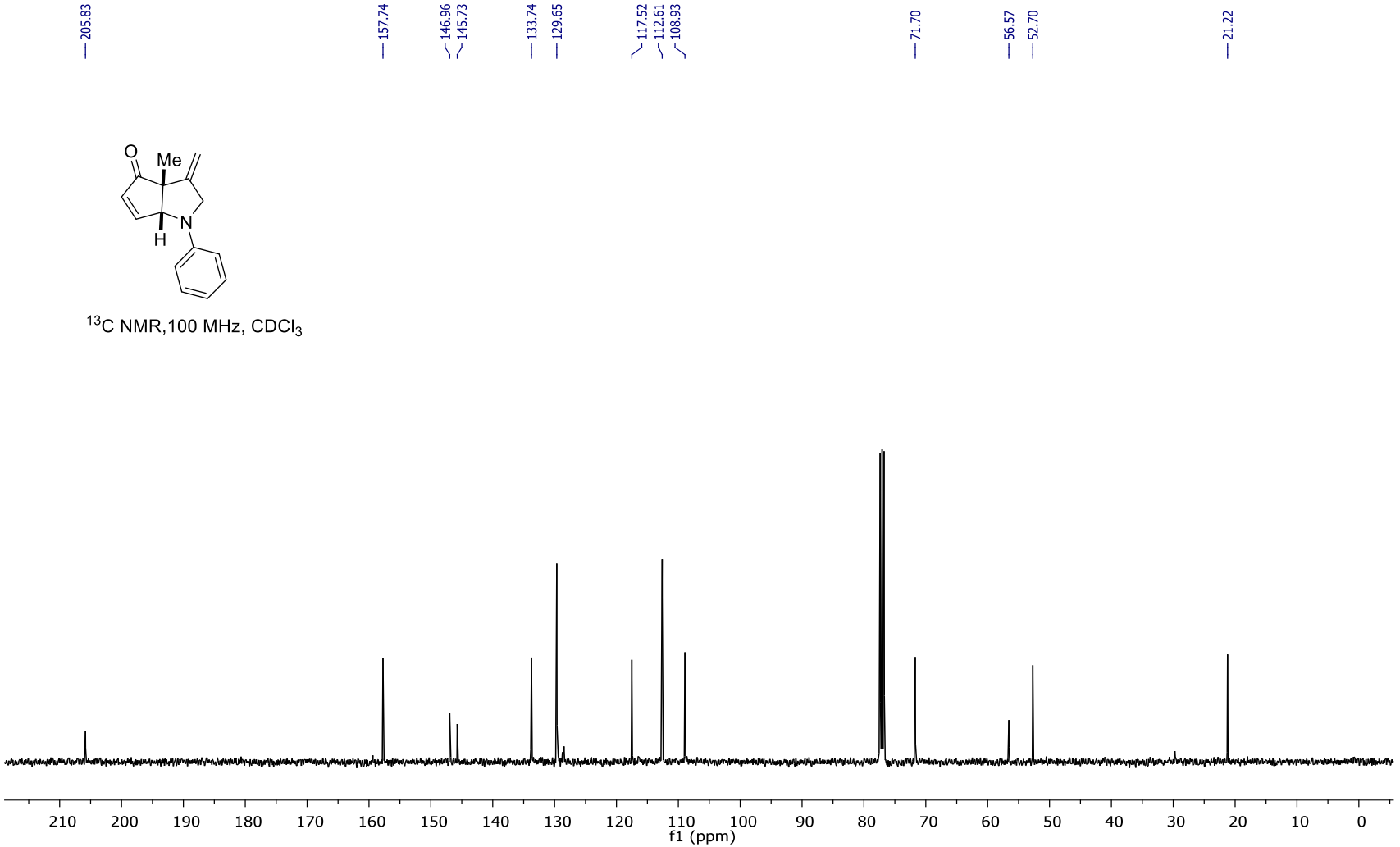


^{19}F NMR, 377 MHz, $CDCl_3$

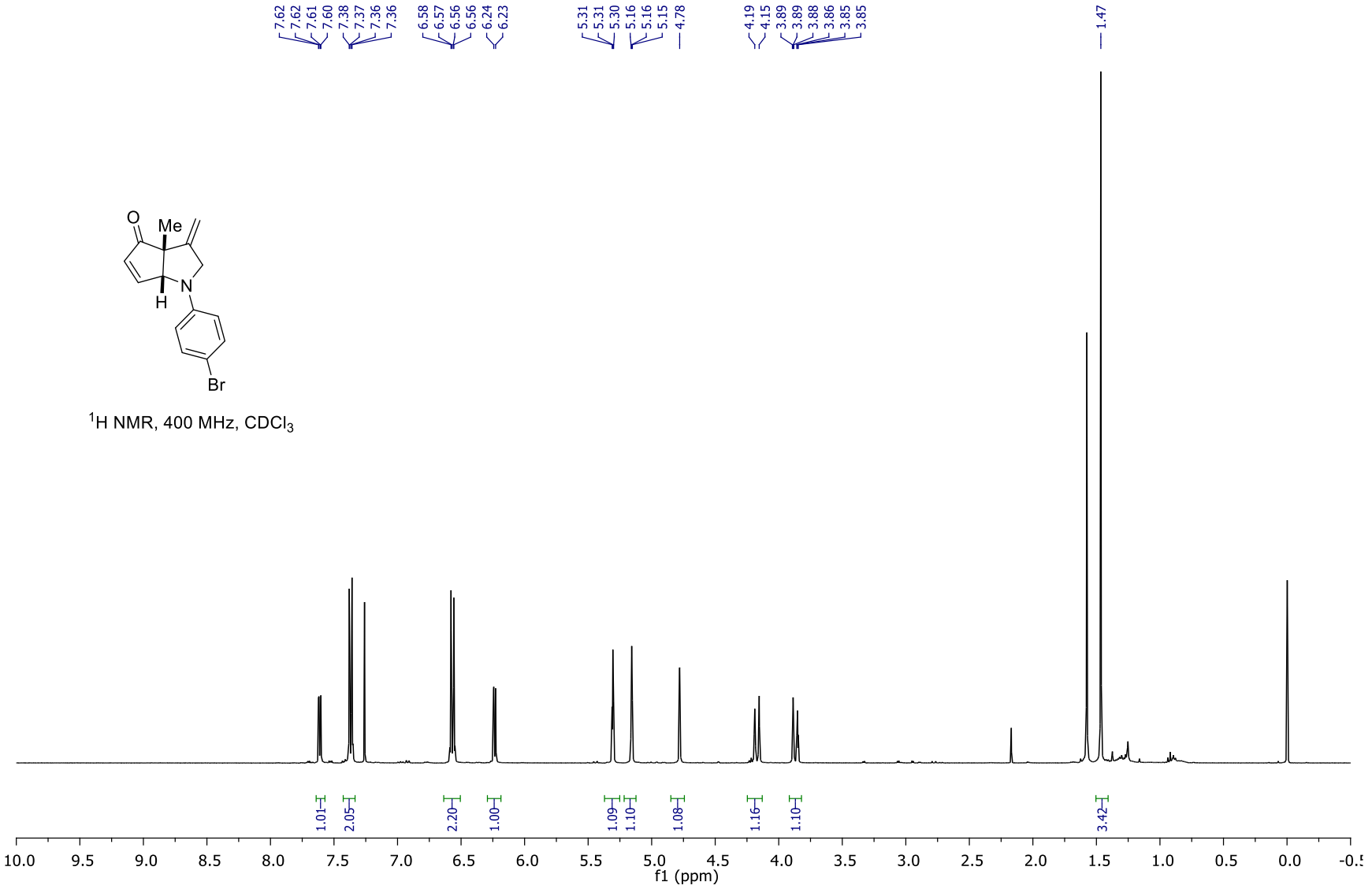
3a-Methyl-3-methylene-1-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4k)



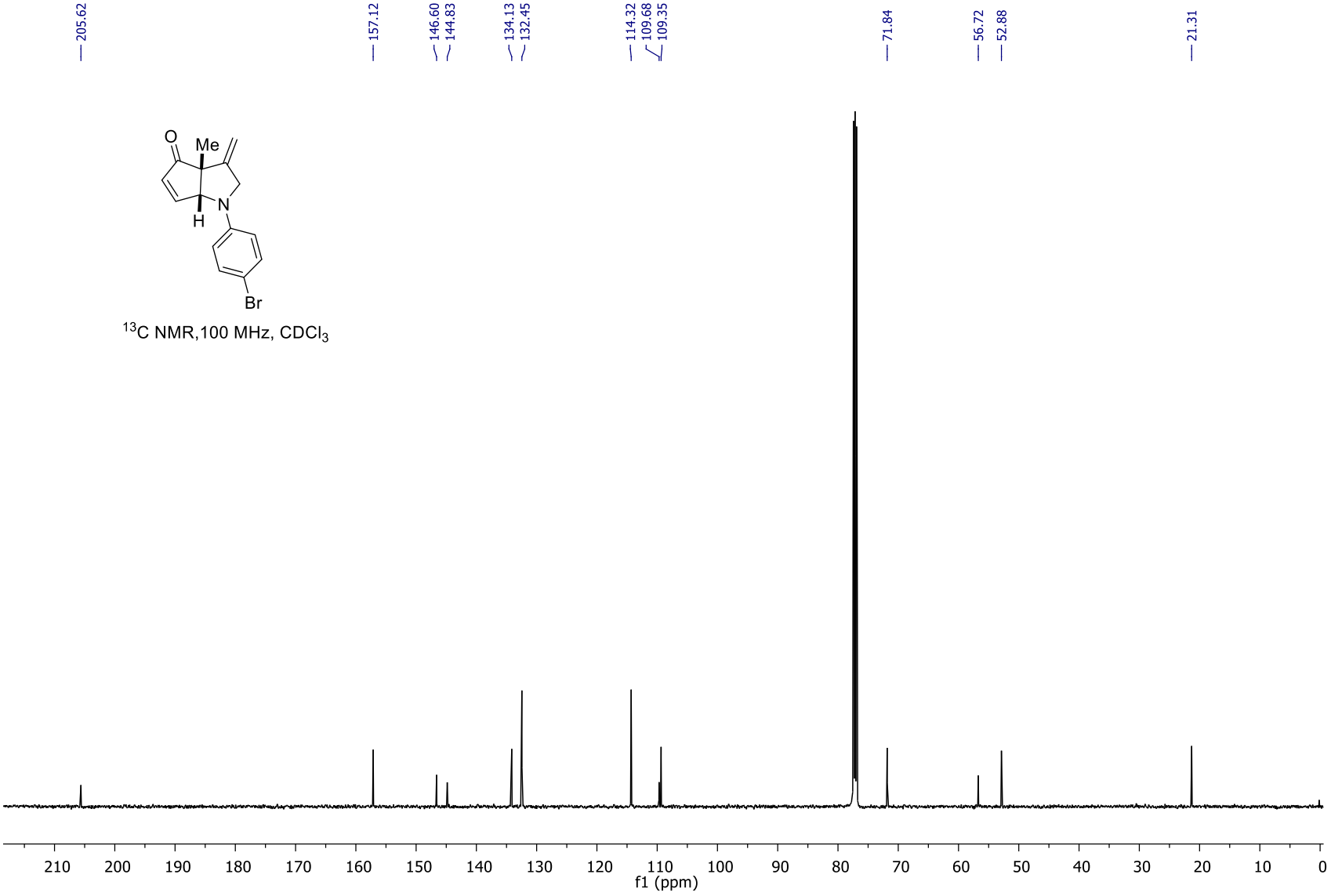
3a-Methyl-3-methylene-1-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4k)



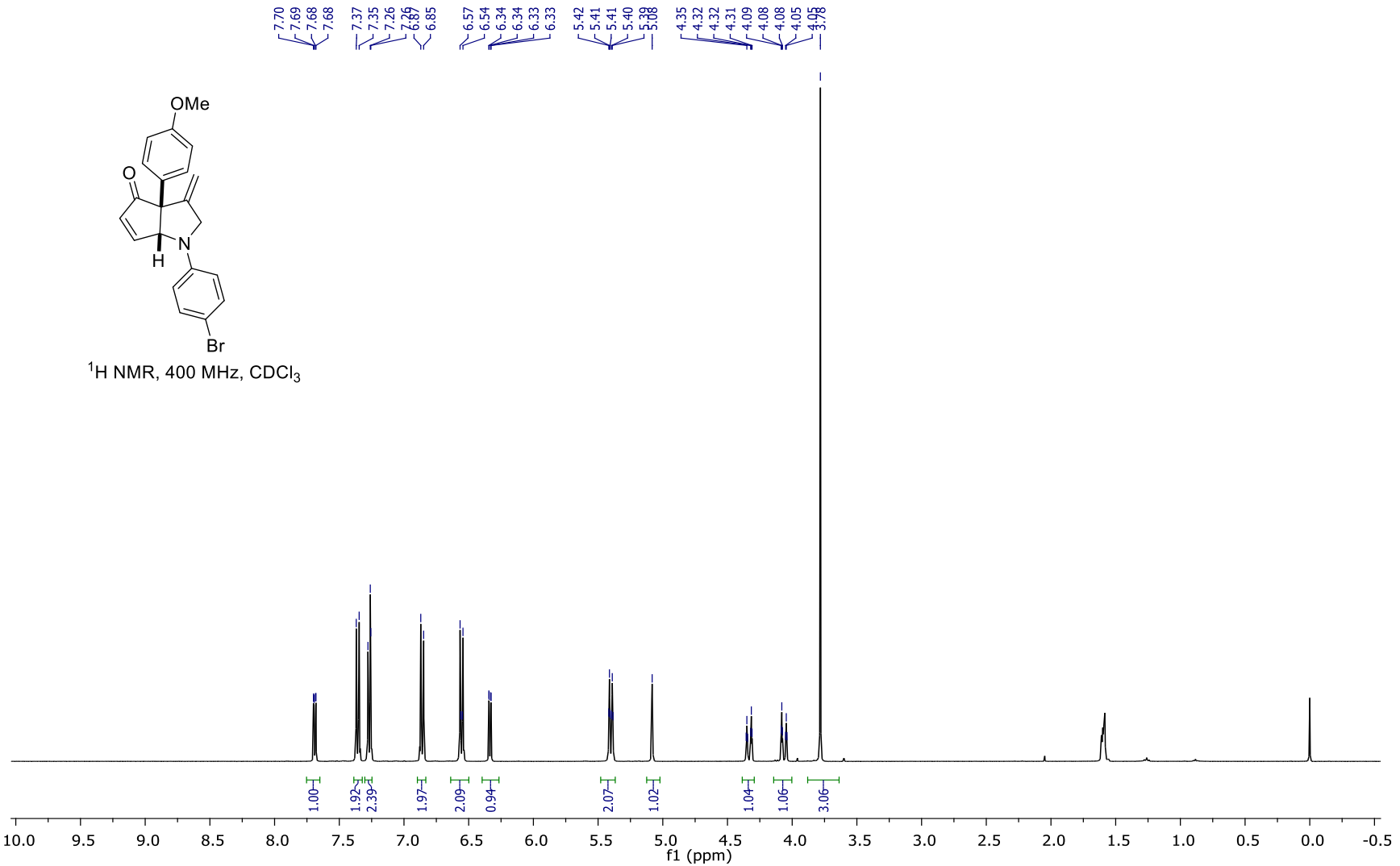
1-(4-Bromophenyl)-3a-methyl-3-methylene-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4l)



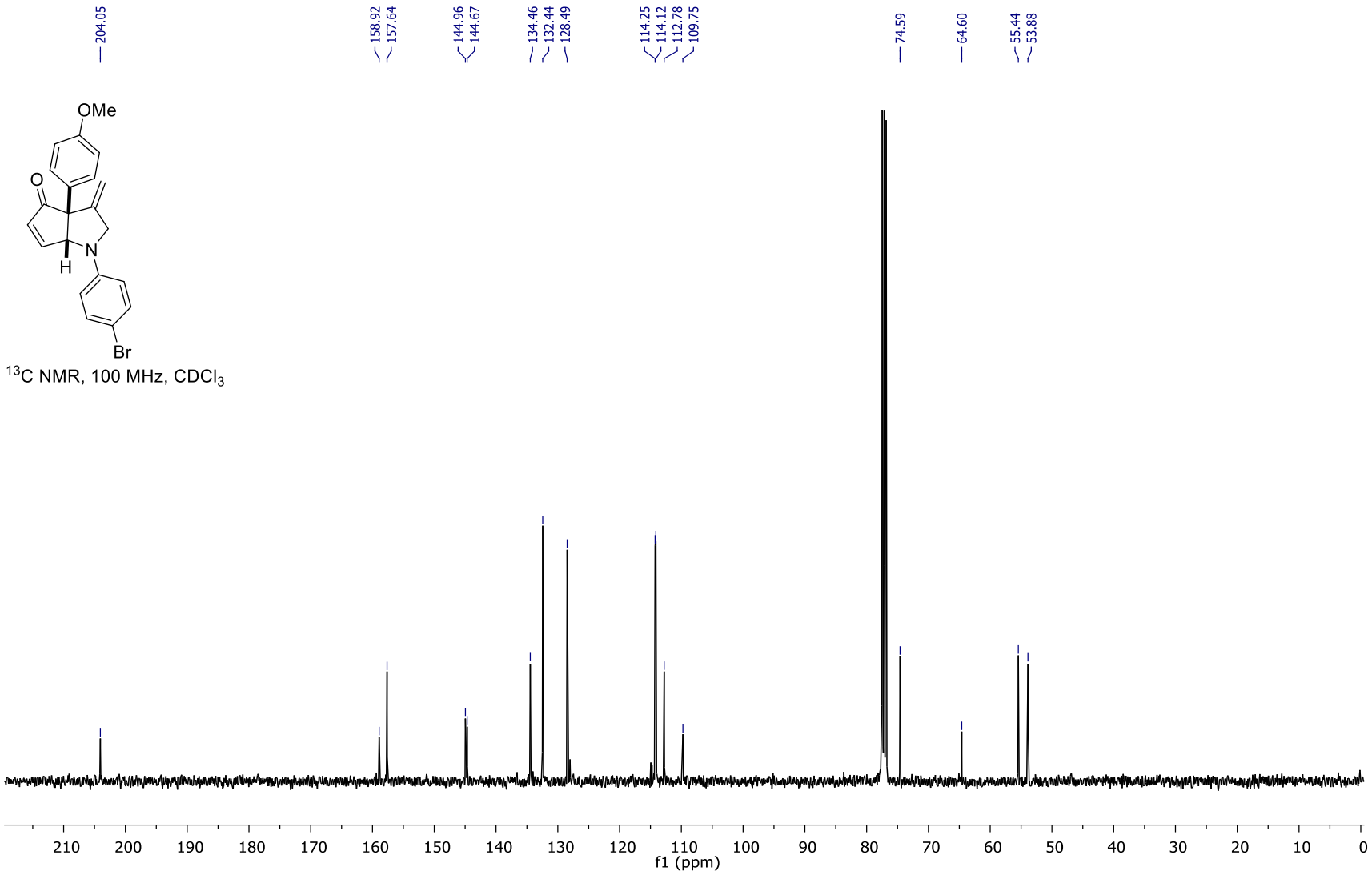
1-(4-Bromophenyl)-3a-methyl-3-methylene-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4l)



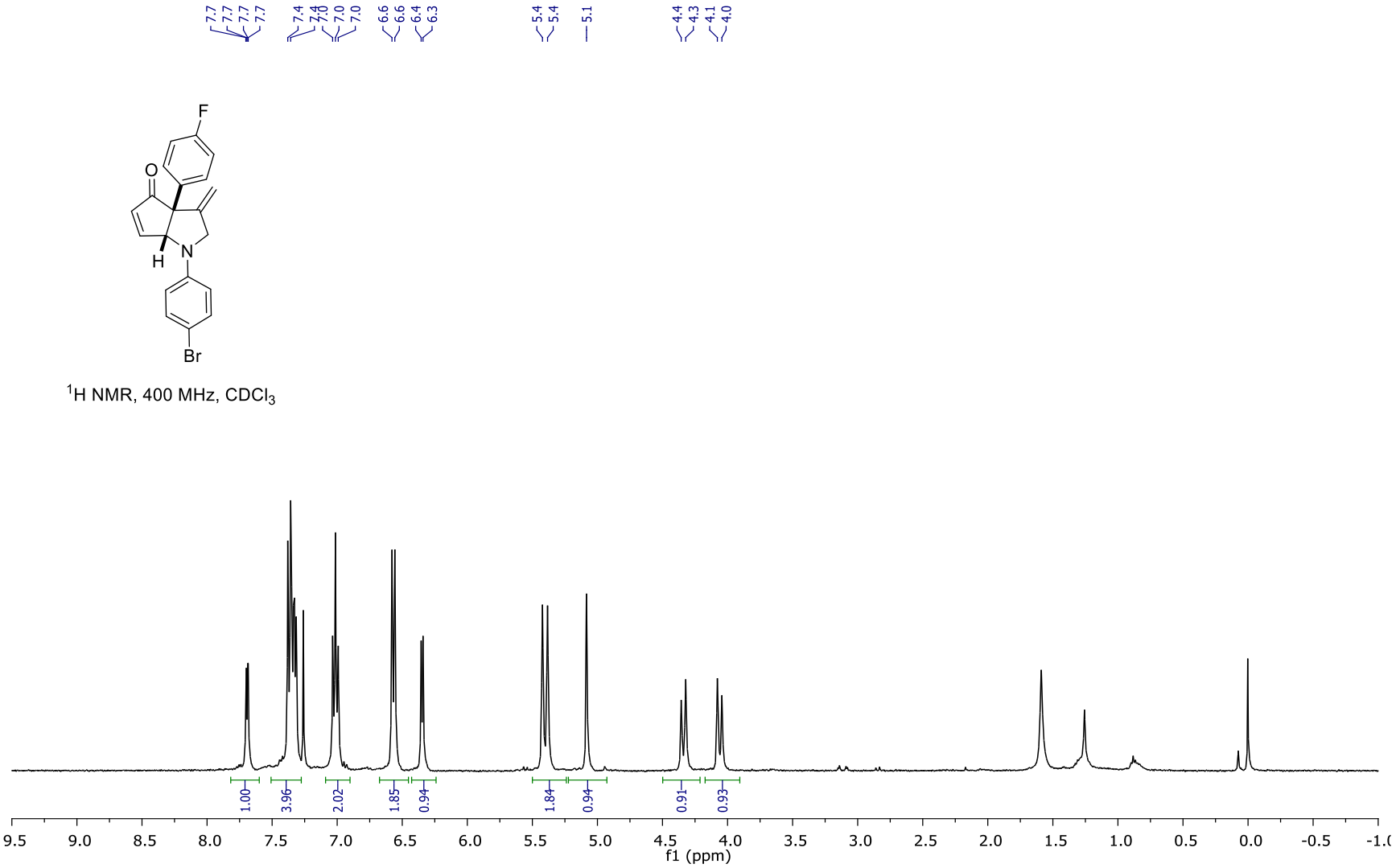
1-(4-Bromophenyl)-3a-(4-methoxyphenyl)-3-methylene-2,3,3a,6a-tetrahydrocyclopenta [*b*] pyrrol-4(1*H*)-one (4m)



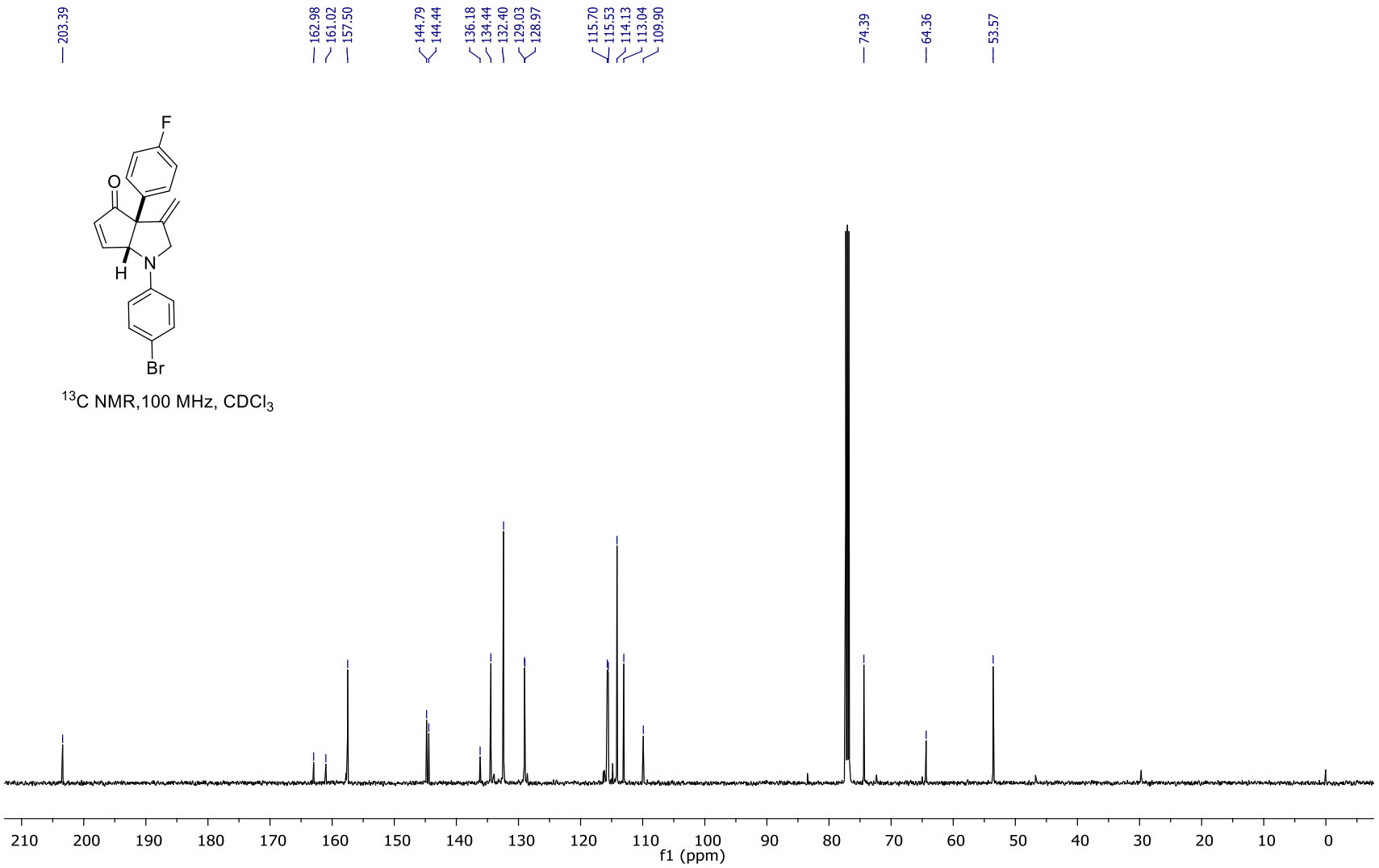
1-(4-Bromophenyl)-3a-(4-methoxyphenyl)-3-methylene-2,3,3a,6a-tetrahydrocyclopenta [*b*] pyrrol-4(1*H*)-one (4m)



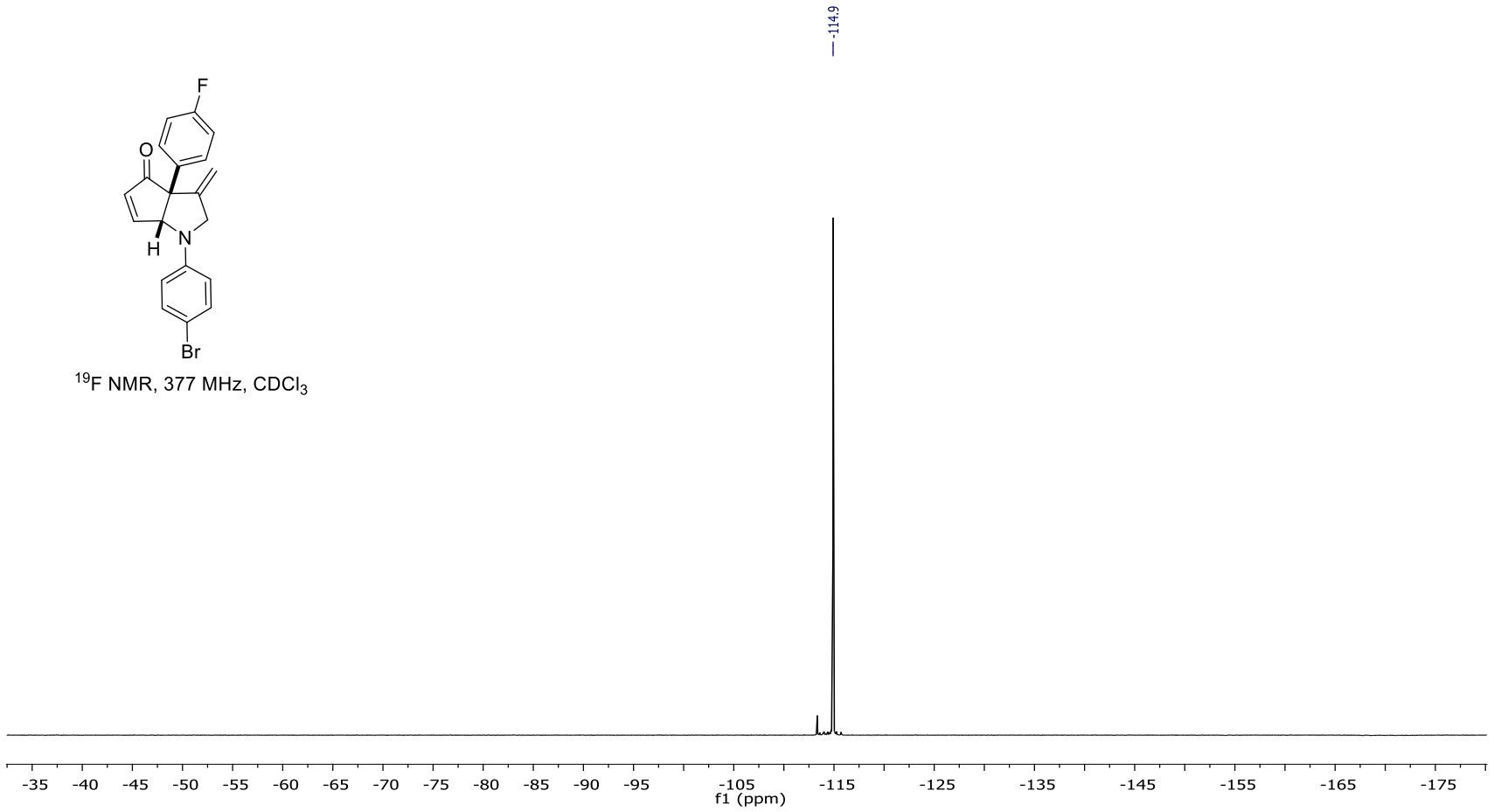
(4-Bromophenyl)-3a-(4-fluorophenyl)-3-methylene-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrro l-4(1*H*)-one (4n)



(4-Bromophenyl)-3a-(4-fluorophenyl)-3-methylene-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrro l-4(1*H*)-one (4n)

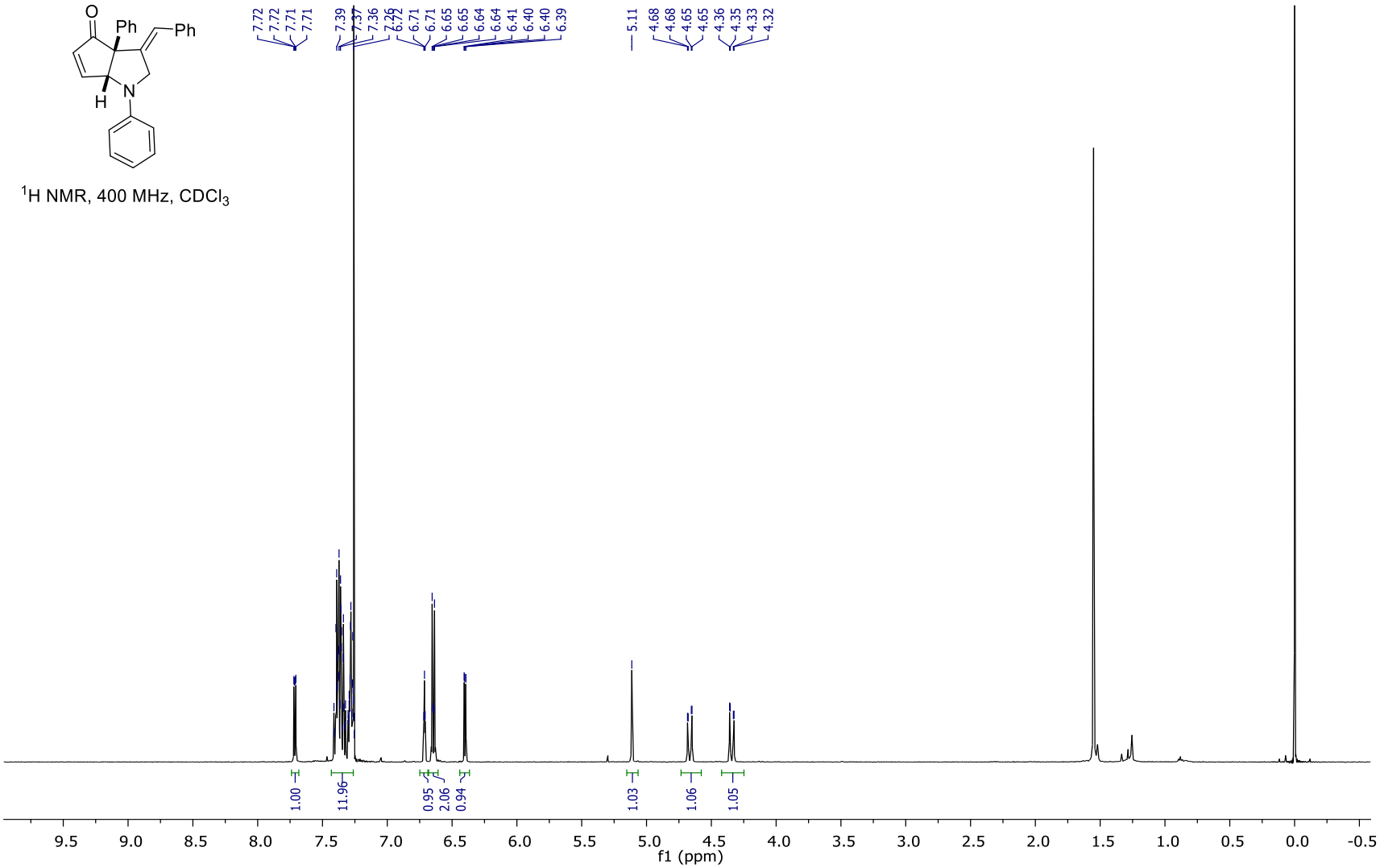


^{19}F Spectrum of Compound (4n)



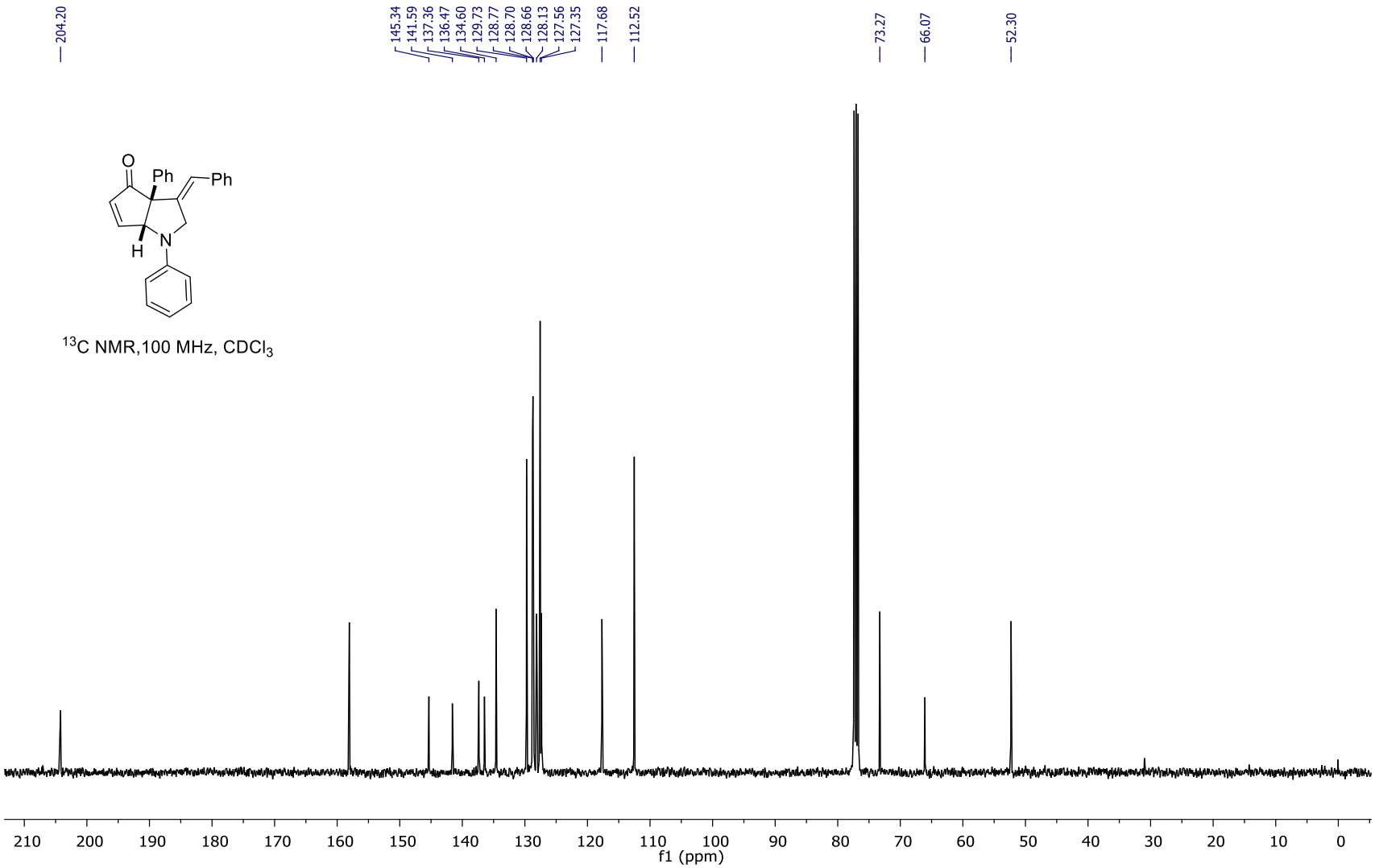
^{19}F NMR, 377 MHz, $CDCl_3$

3-((*Z*)-Benzylidene)-1,3a-diphenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4o)

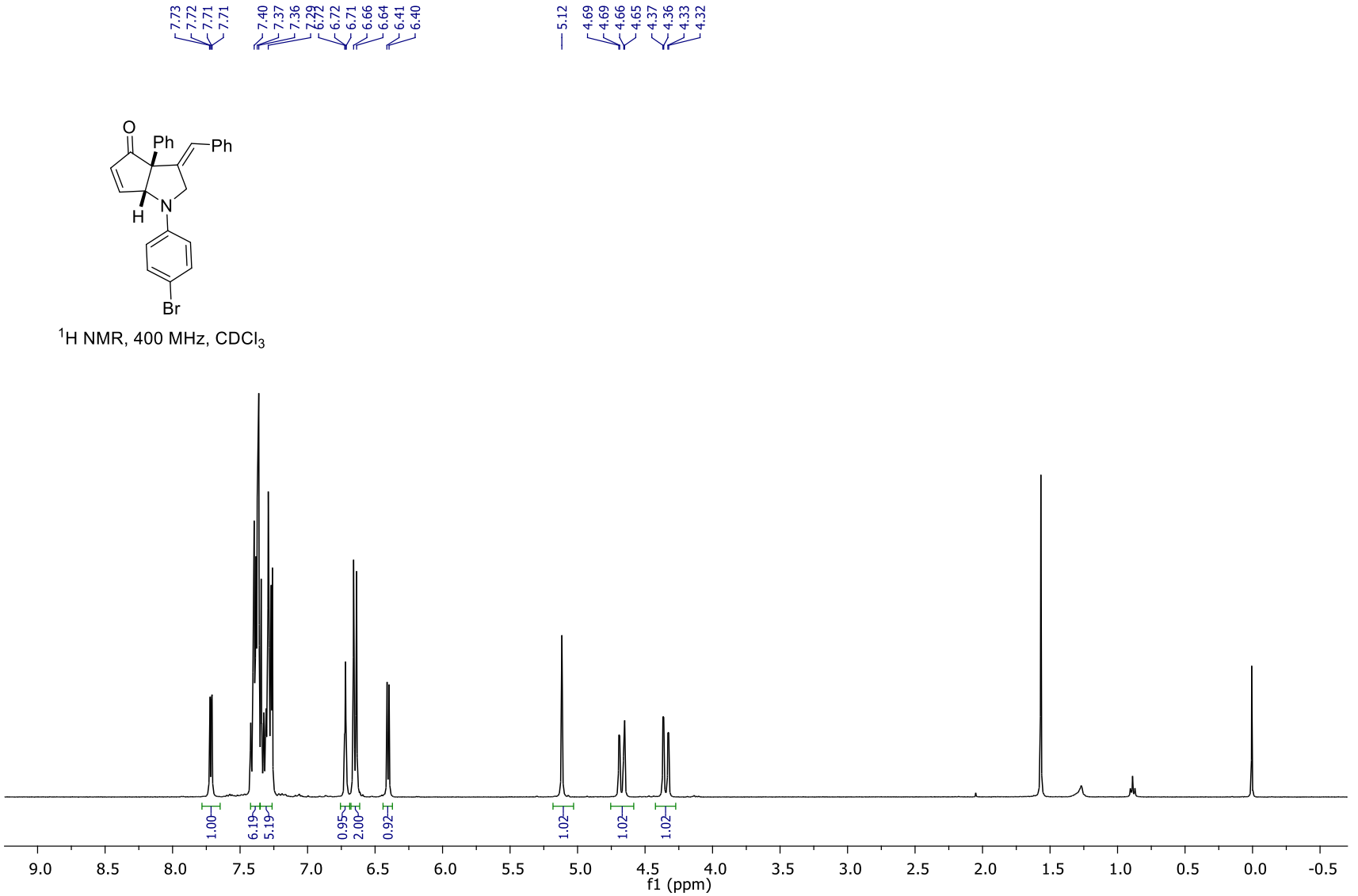


^{1}H NMR, 400 MHz, $CDCl_3$

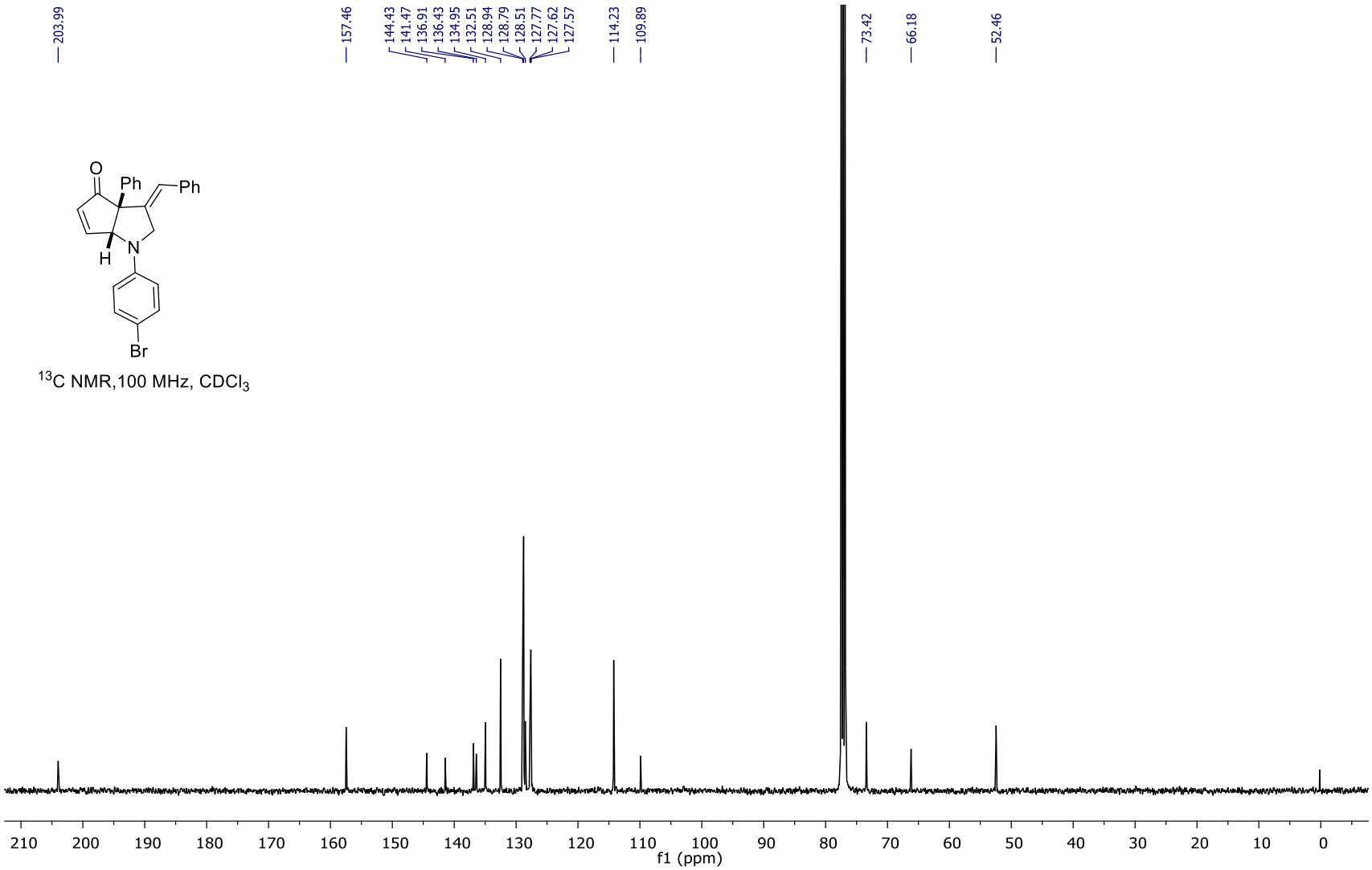
3-((Z)-Benzylidene)-1,3a-diphenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4o)



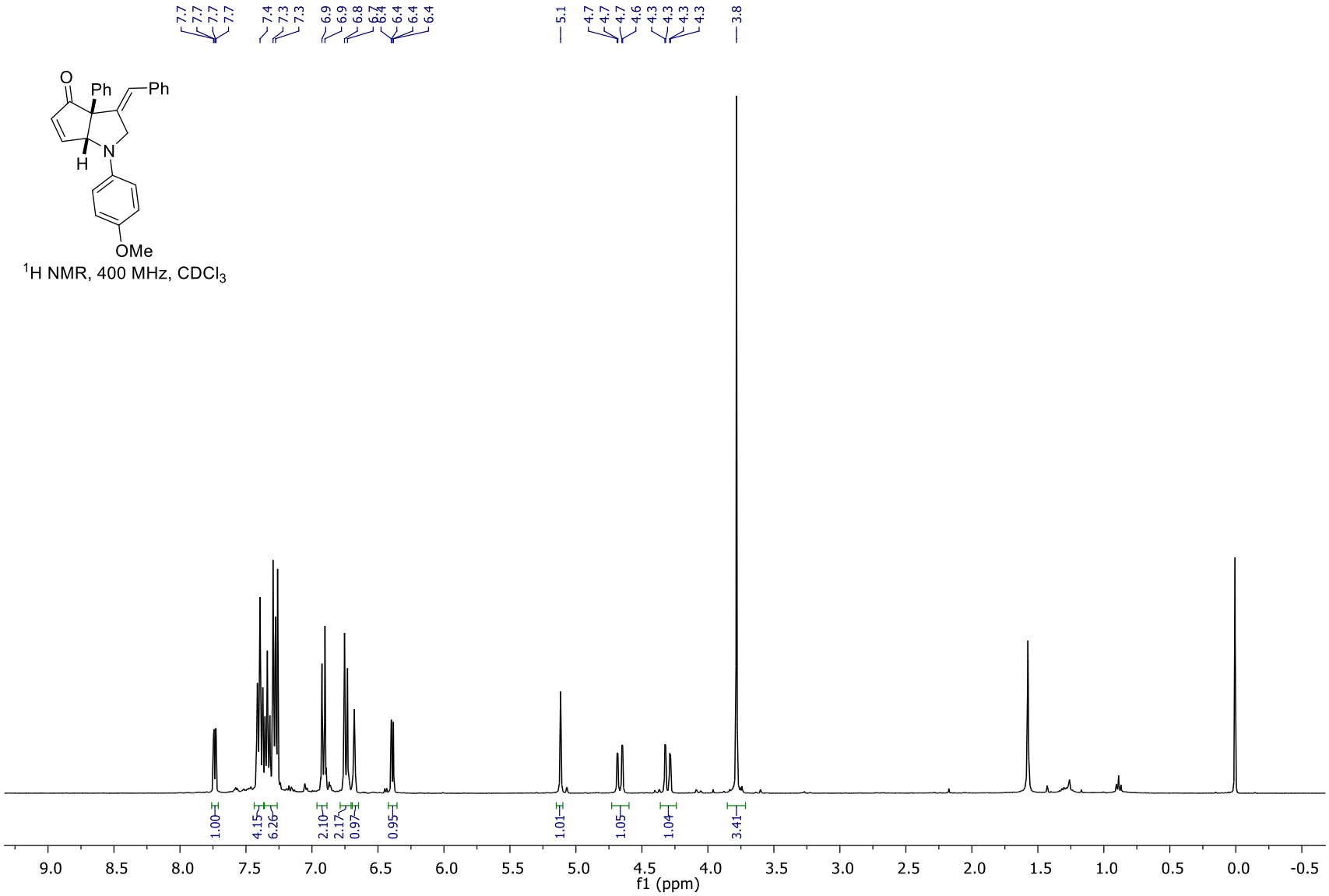
3-((*Z*)-Benzylidene)-1-(4-bromophenyl)-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4p)



3-((*Z*)-Benzylidene)-1-(4-bromophenyl)-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4p)

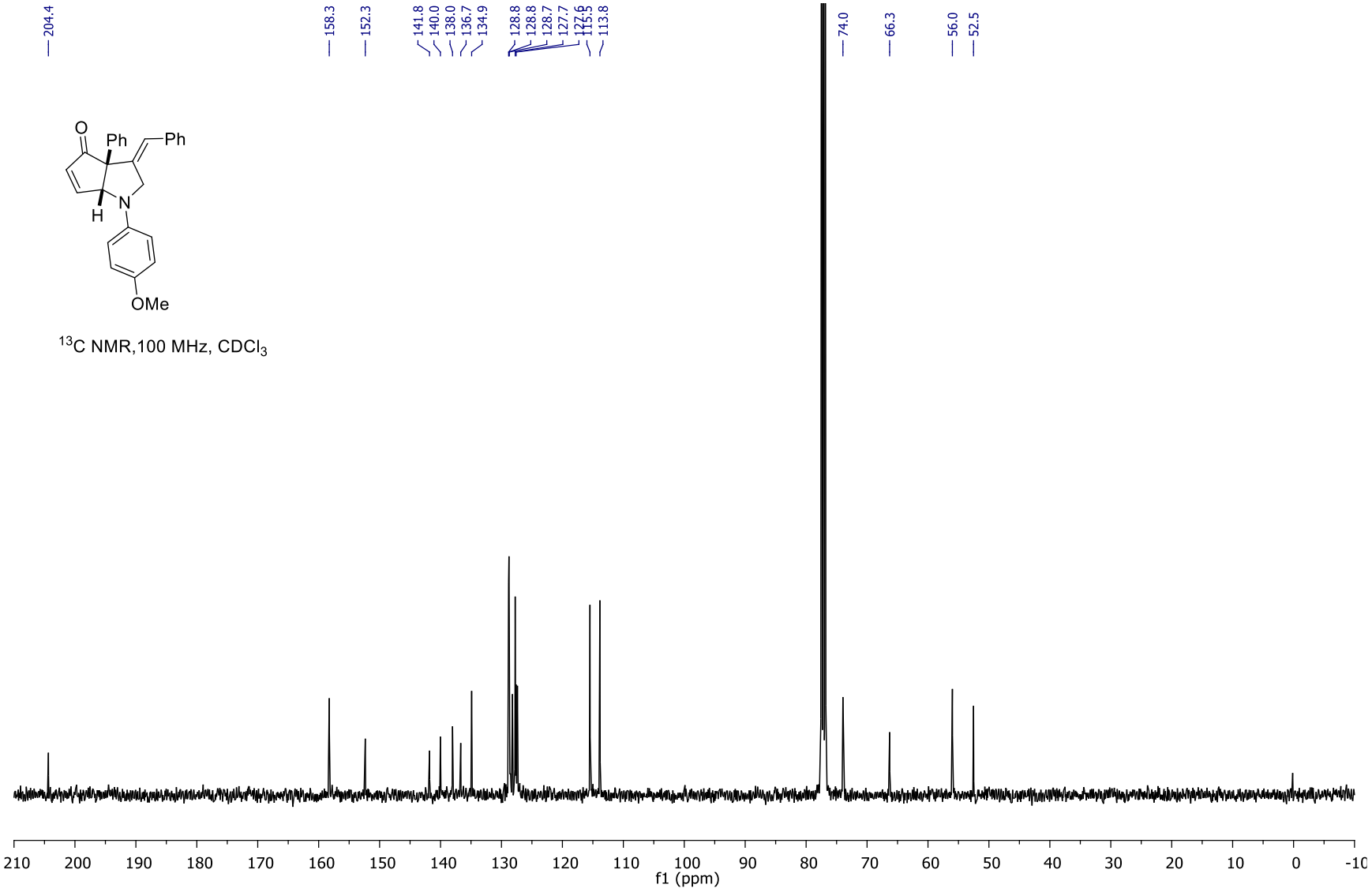


3-((*Z*)-Benzylidene)-1-(4-methoxyphenyl)-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrr ol-4(1*H*)-one (4q)

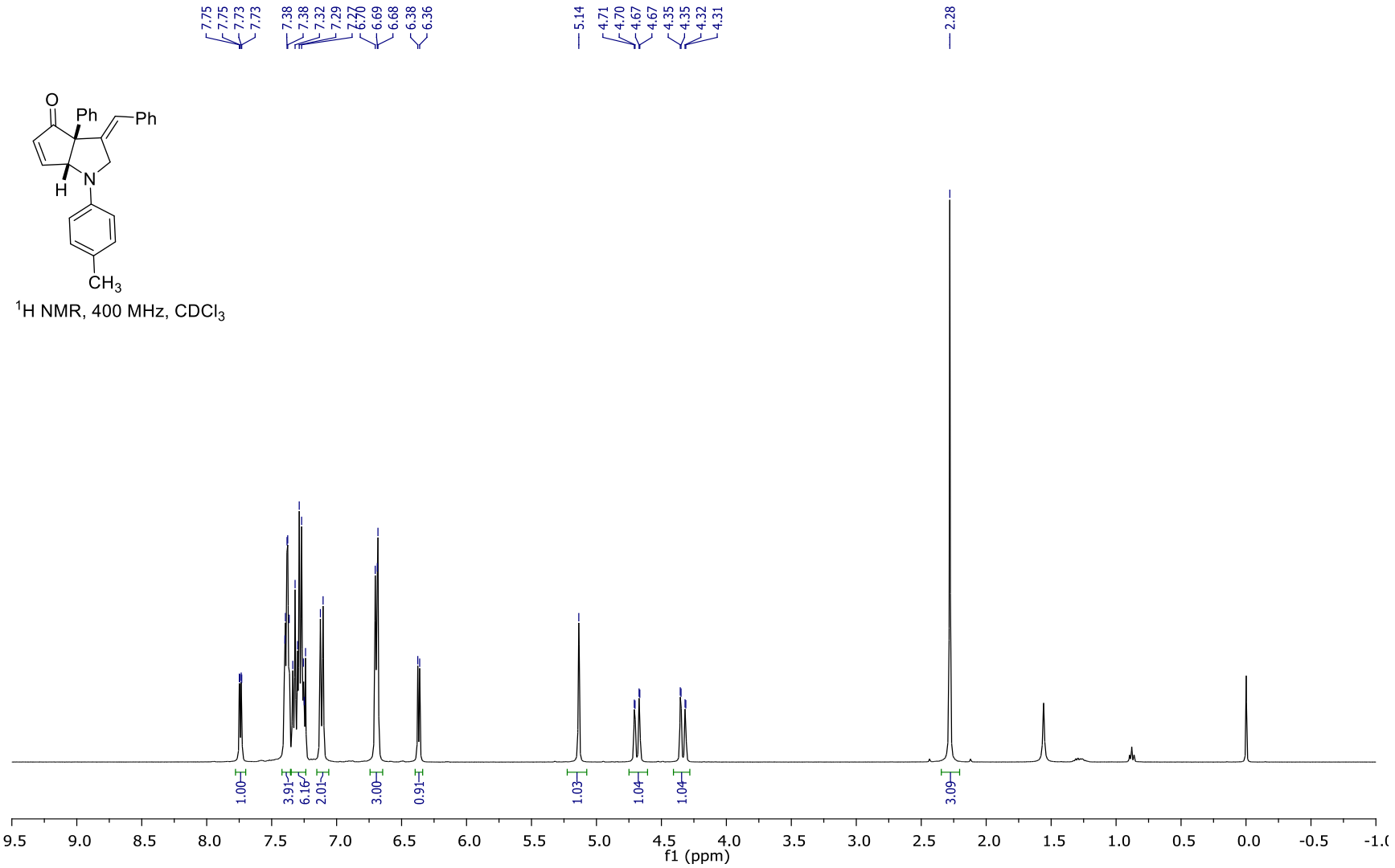


^{1}H NMR, 400 MHz, $CDCl_3$

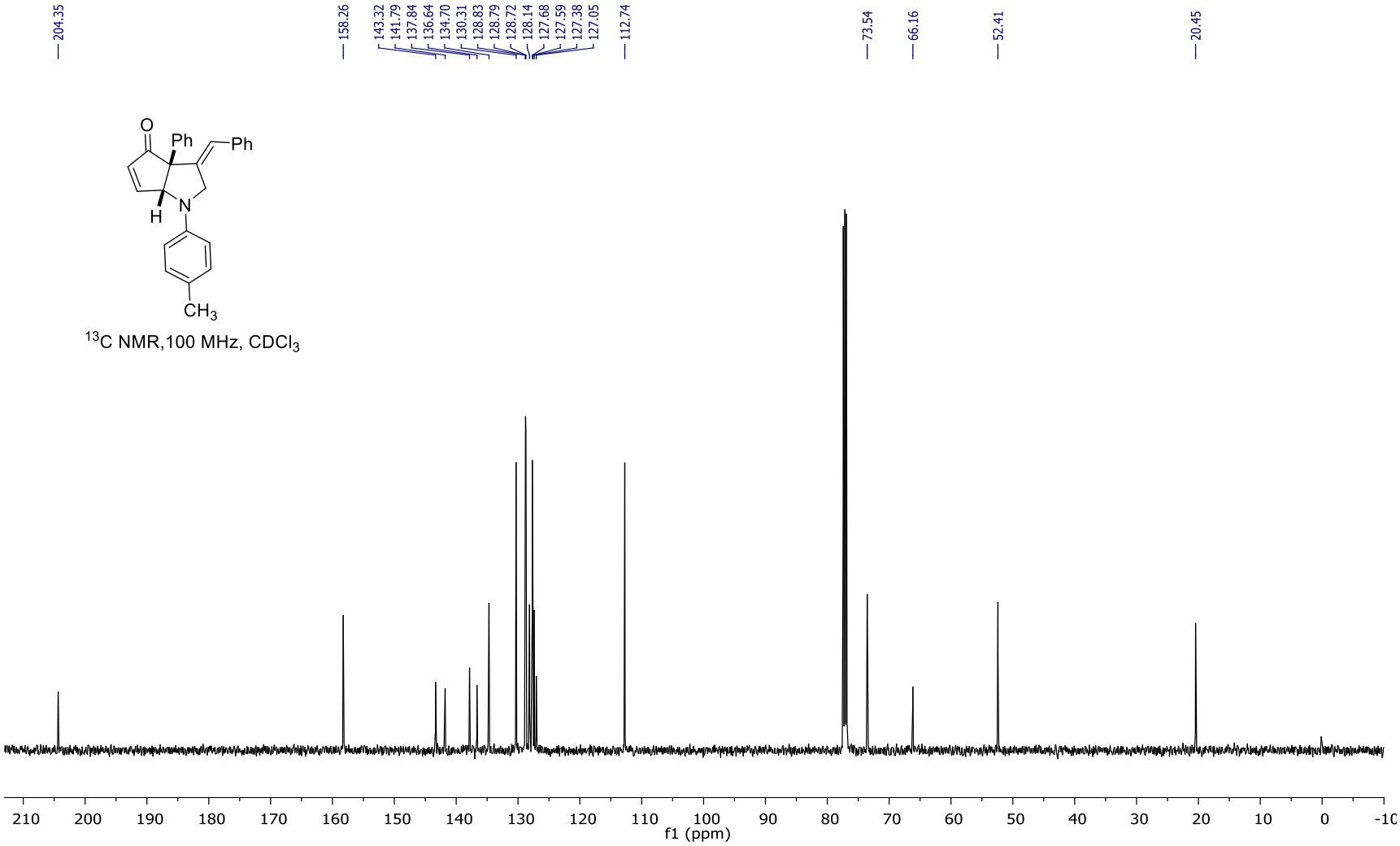
3-((*Z*)-Benzylidene)-1-(4-methoxyphenyl)-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrr ol-4(1*H*)-one (4q)



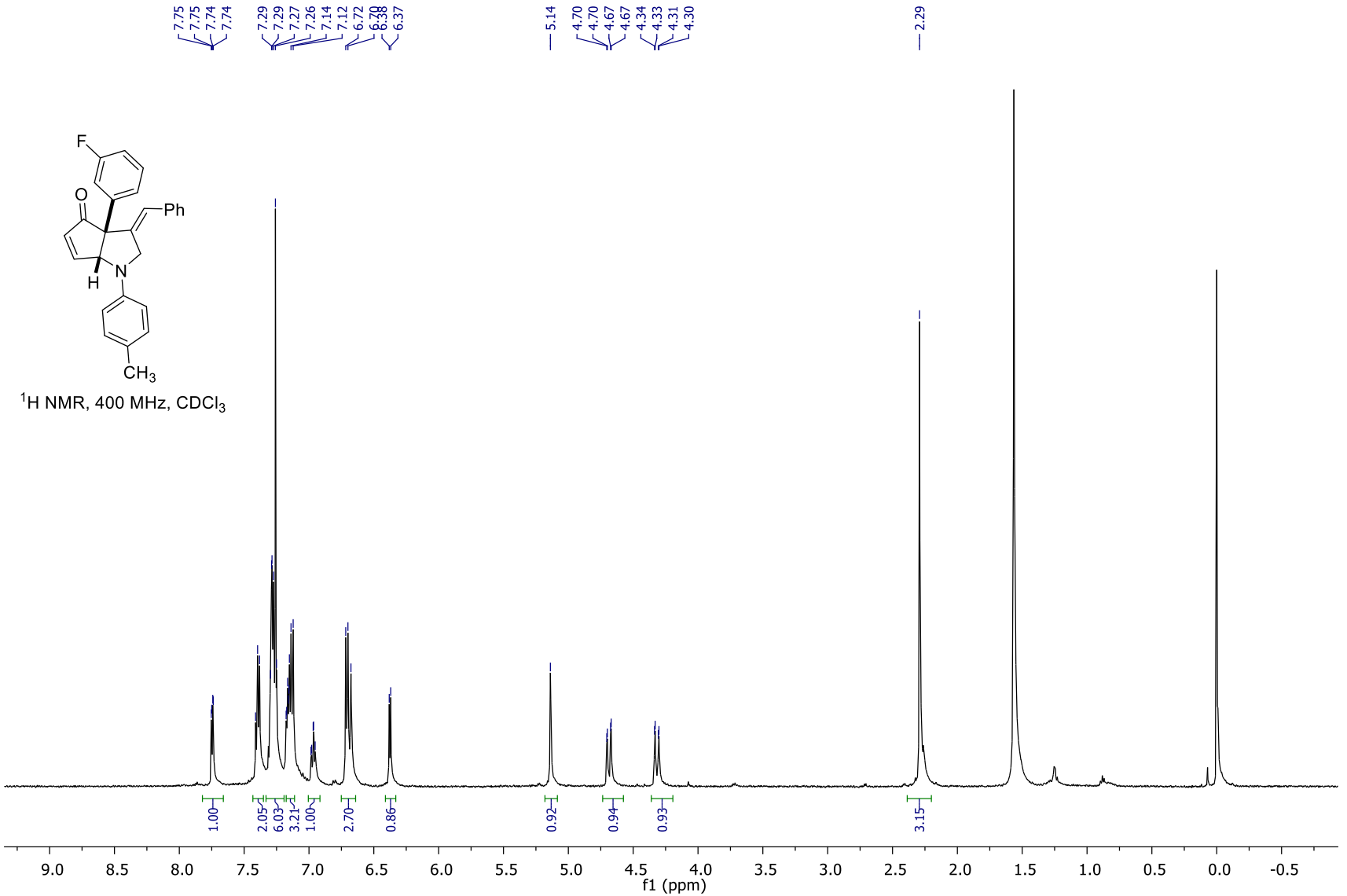
3-((*Z*)-Benzylidene)-3a-phenyl-1-(*p*-tolyl)-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*) one (4r)



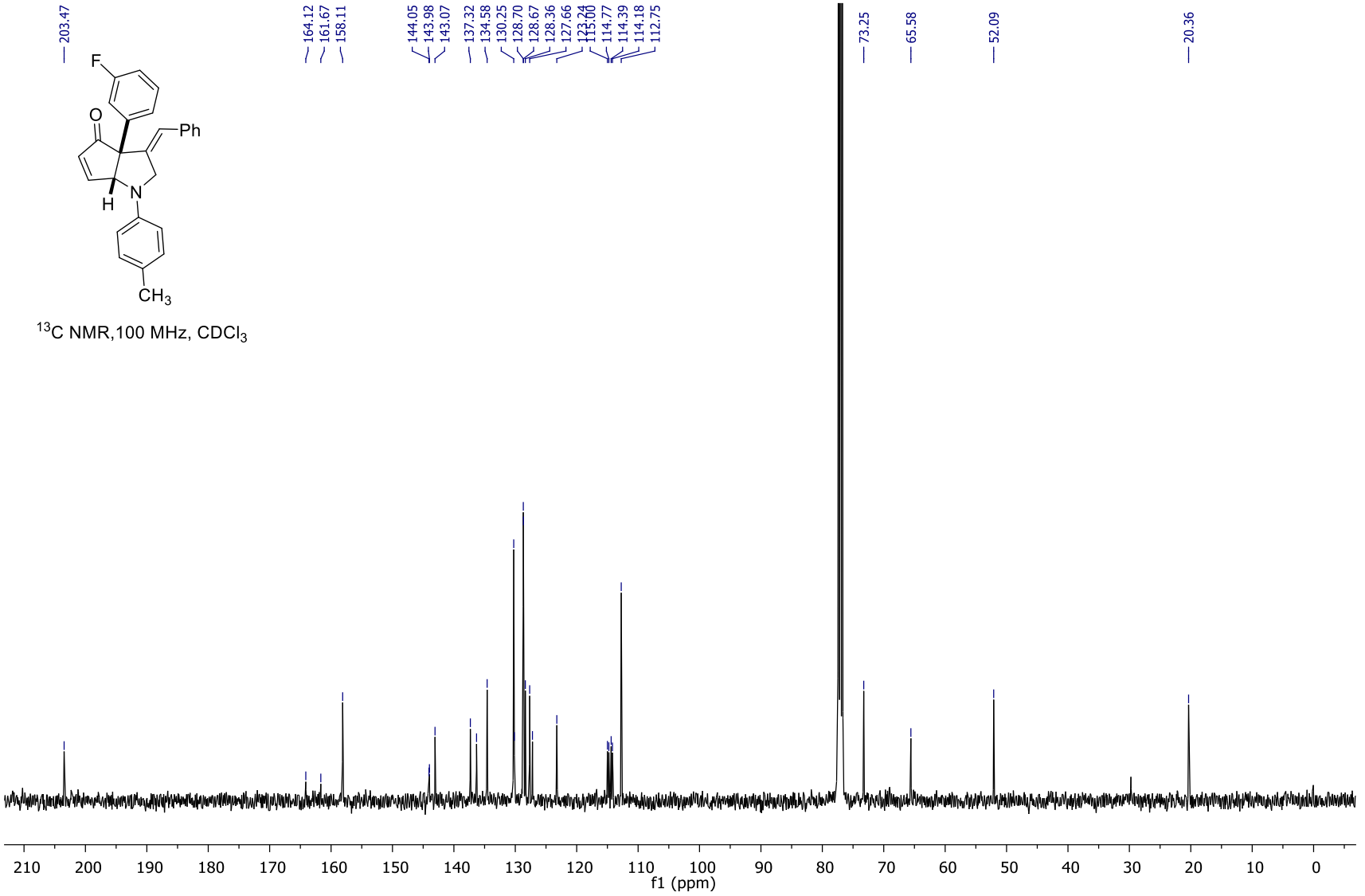
3-((*Z*)-Benzylidene)-3a-phenyl-1-(*p*-tolyl)-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*) one (4r)



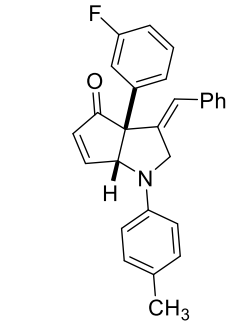
3-((*Z*)-Benzylidene)-3a-(3-fluorophenyl)-1-(*p*-tolyl)-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrro l-4(1*H*)-one (4s)



3-((*Z*)-Benzylidene)-3a-(3-fluorophenyl)-1-(*p*-tolyl)-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrro l-4(1*H*)-one (4s)

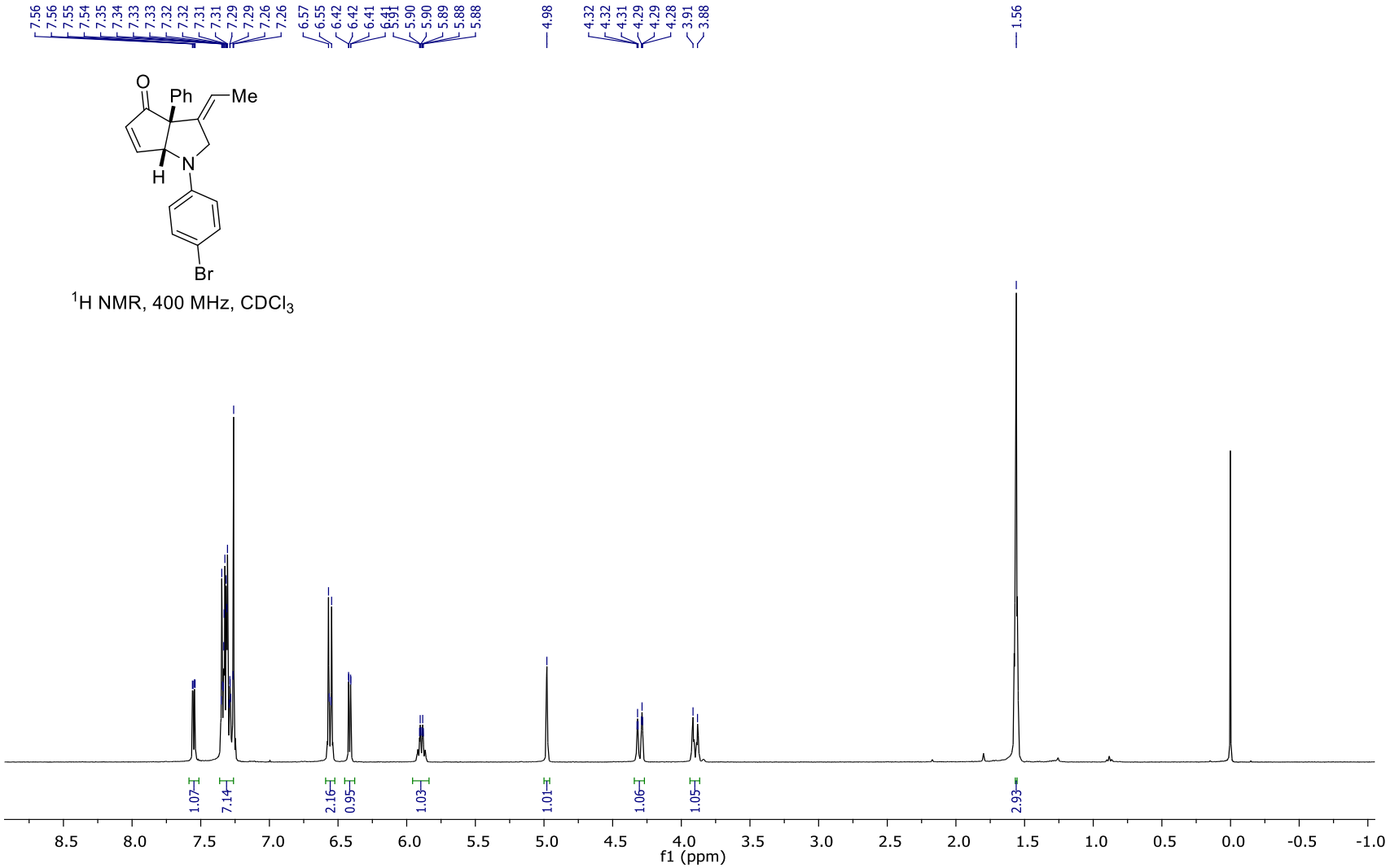


^{19}F Spectrum of 3-((*Z*)-Benzylidene)-3a-(3-fluorophenyl)-1-(*p*-tolyl)-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrro l-4(1*H*)-one (4s)

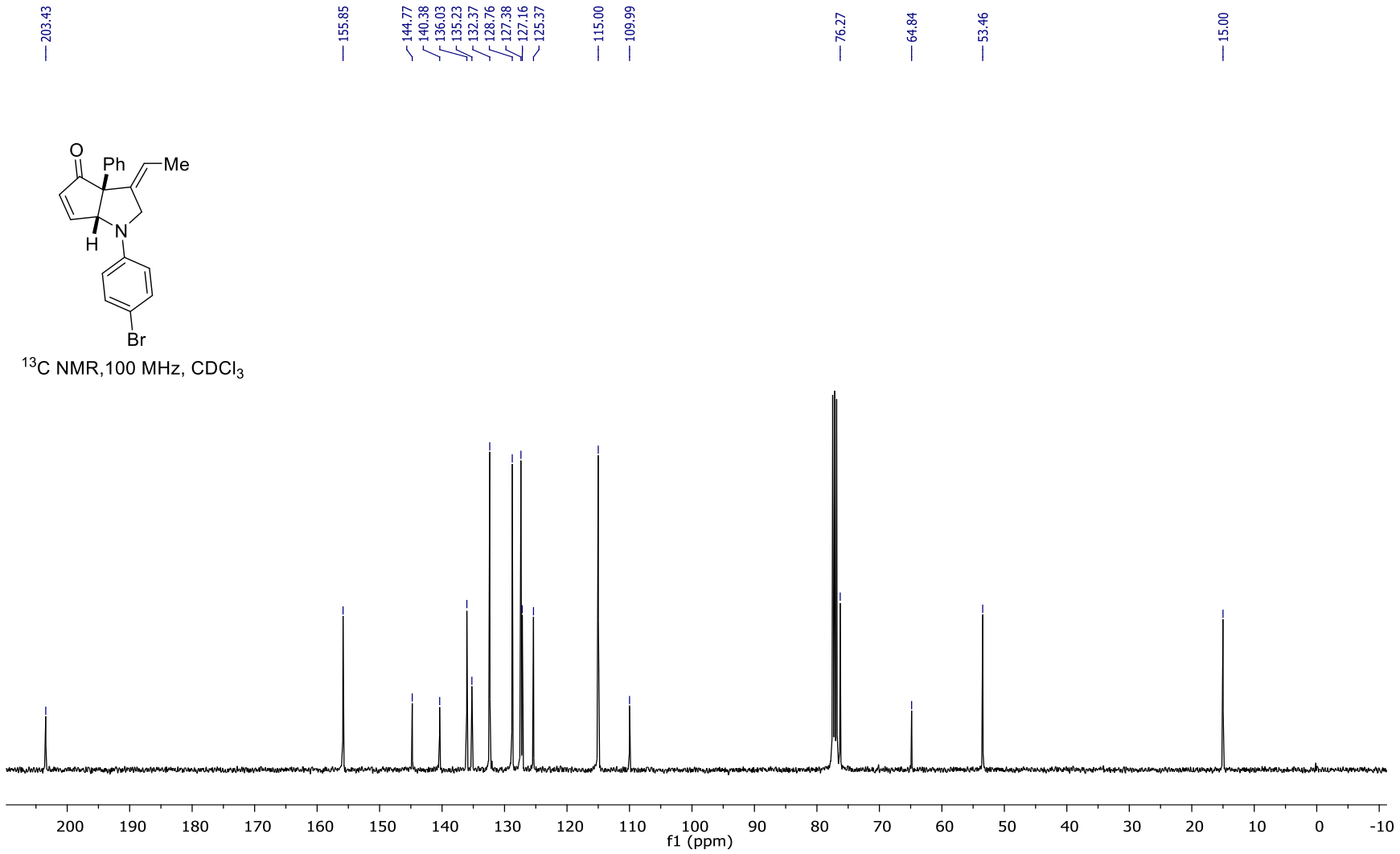


^{19}F NMR, 377 MHz, $CDCl_3$

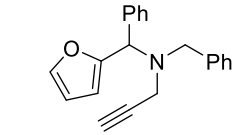
(*Z*)-1-(4-Bromophenyl)-3-ethylidene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4t)



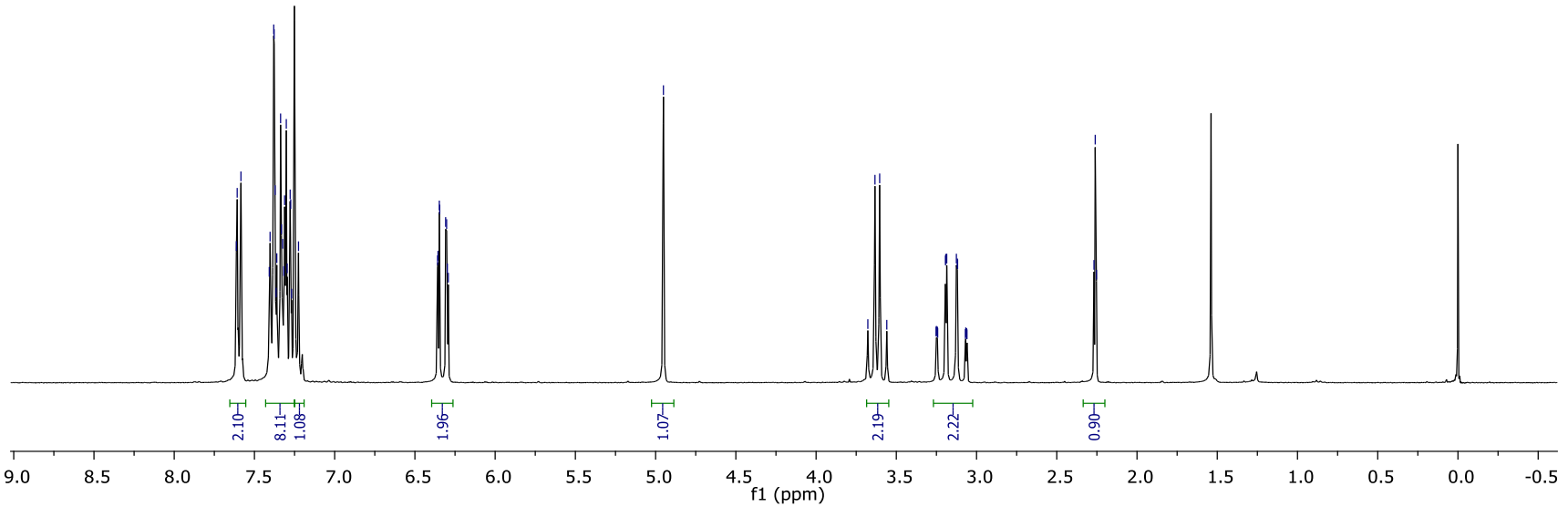
(*Z*)-1-(4-Bromophenyl)-3-ethylidene-3a-phenyl-2,3,3a,6a-tetrahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (4t)



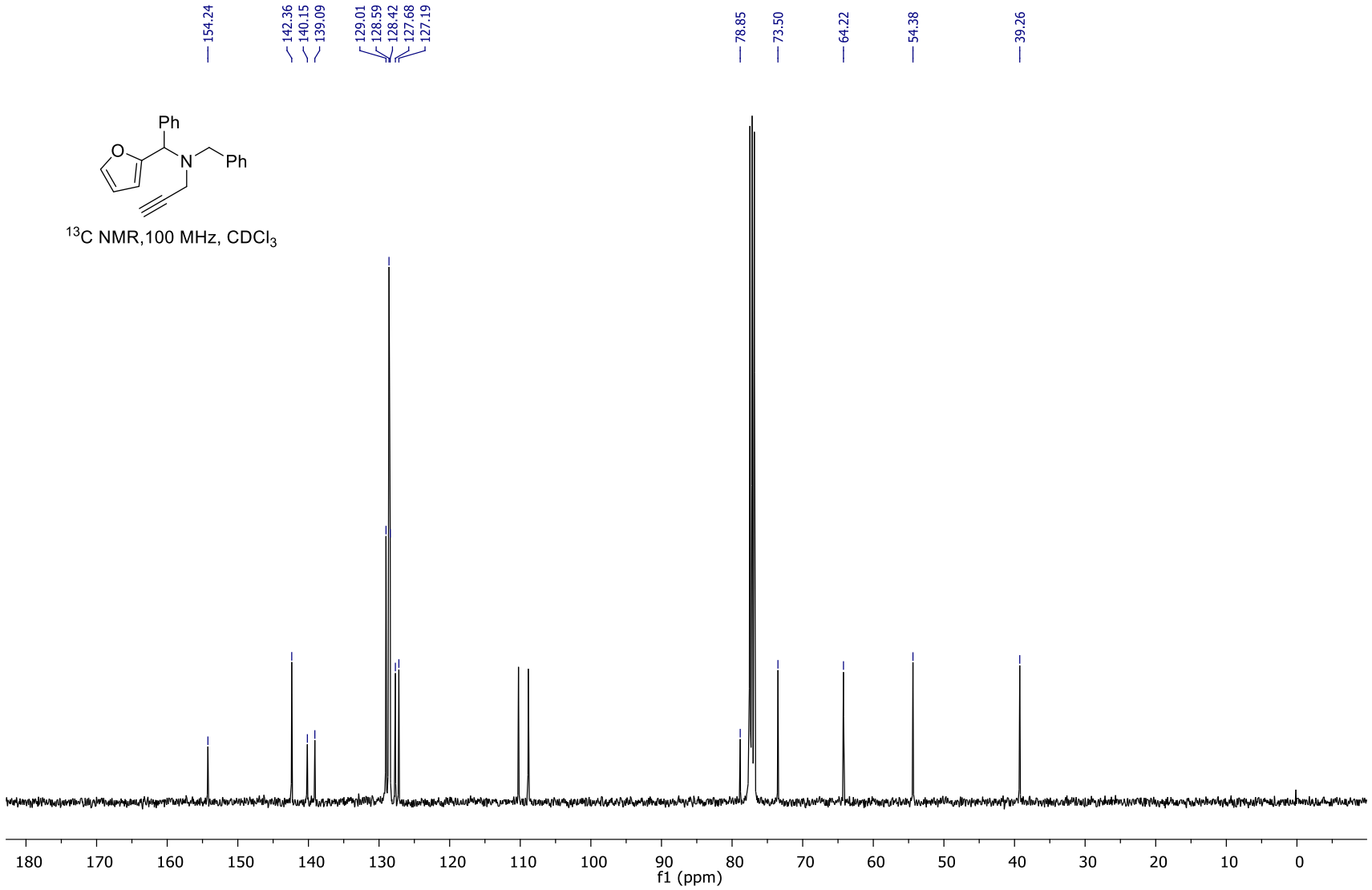
_N_-Benzyl-_N_-(furan-2-yl(phenyl)methyl)prop-2-yn-1-amine (4u′)



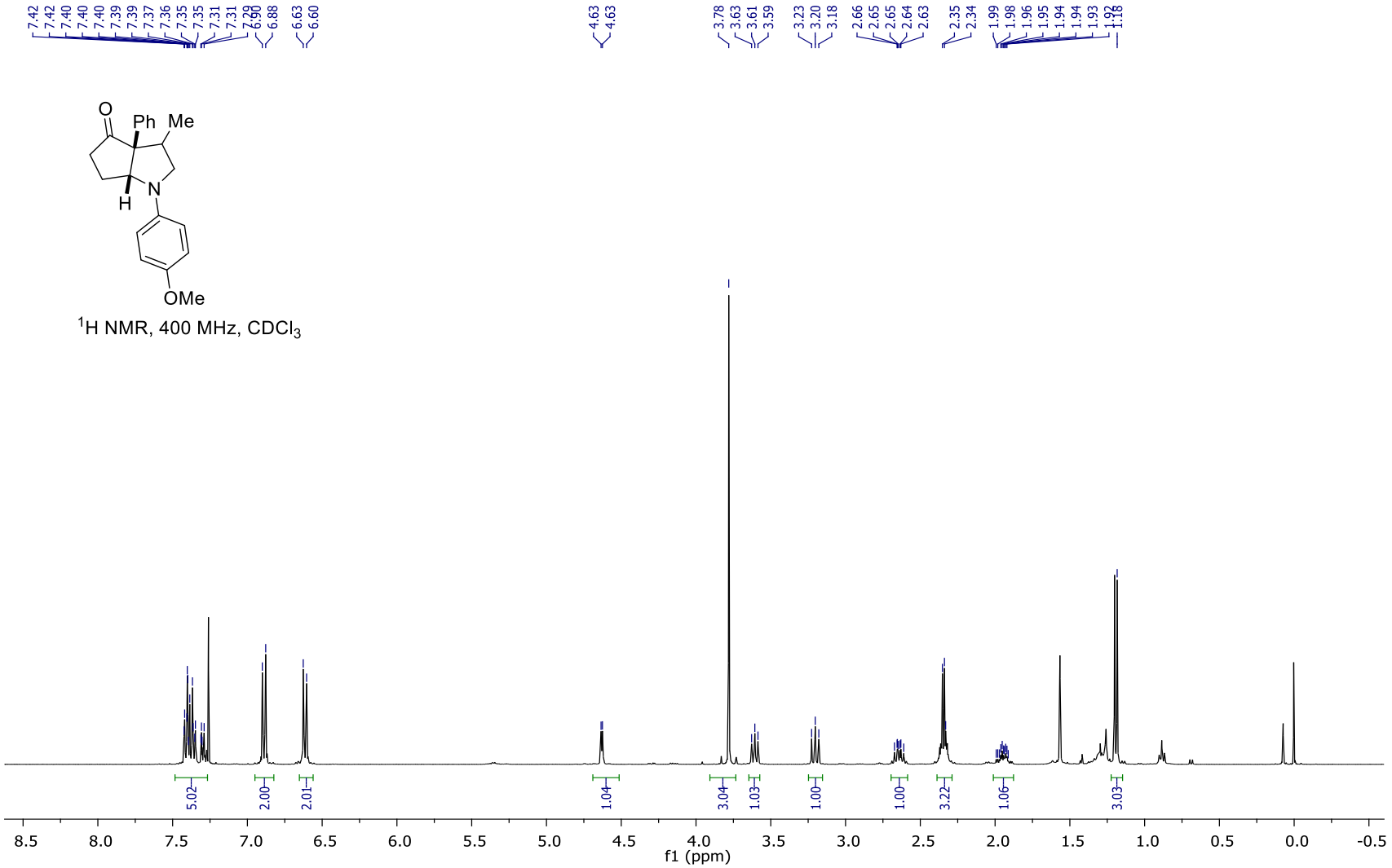
^{1}H NMR, 300 MHz, $CDCl_3$



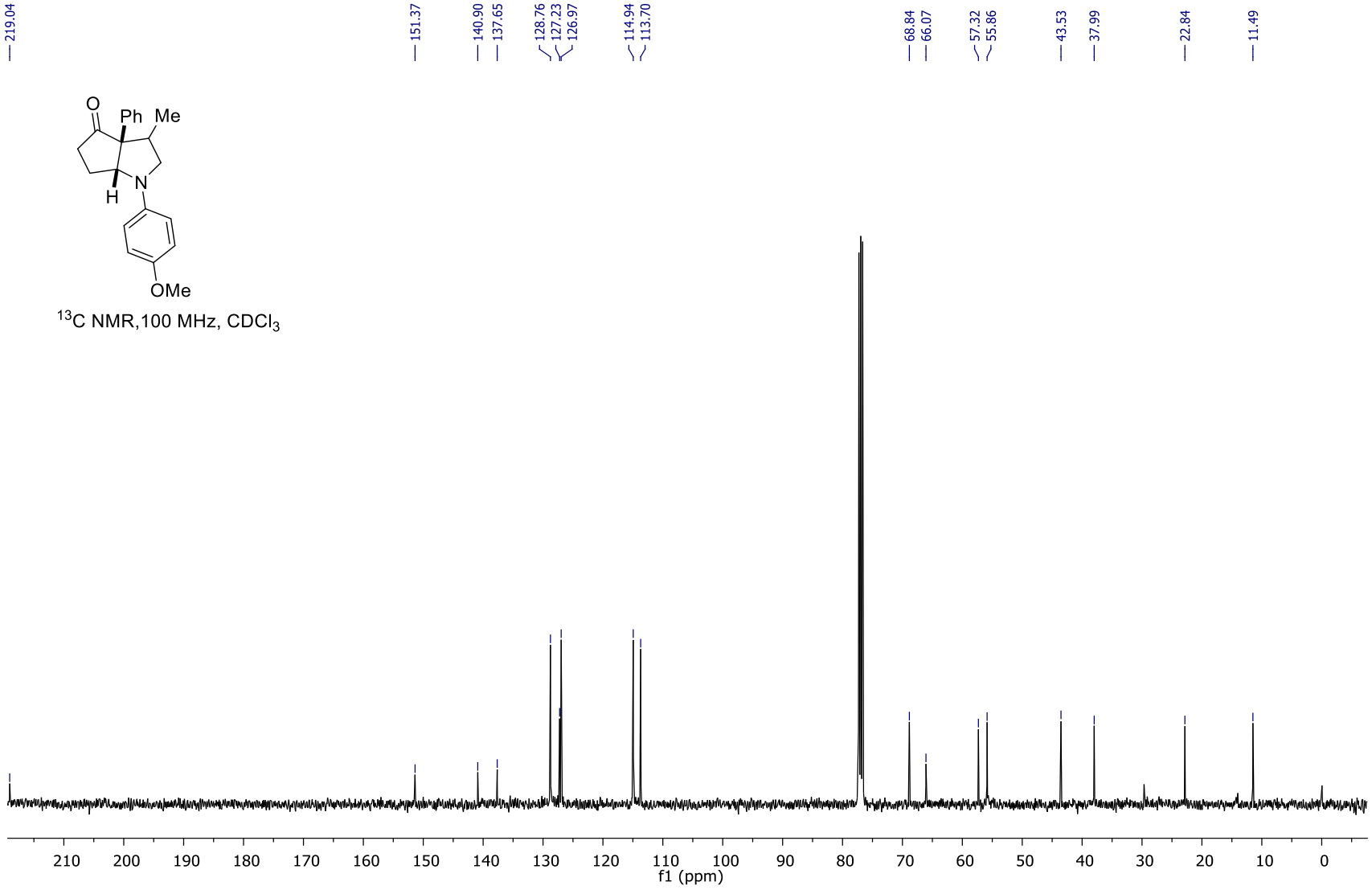
_N_-Benzyl-_N_-(furan-2-yl(phenyl)methyl)prop-2-yn-1-amine (4u′)



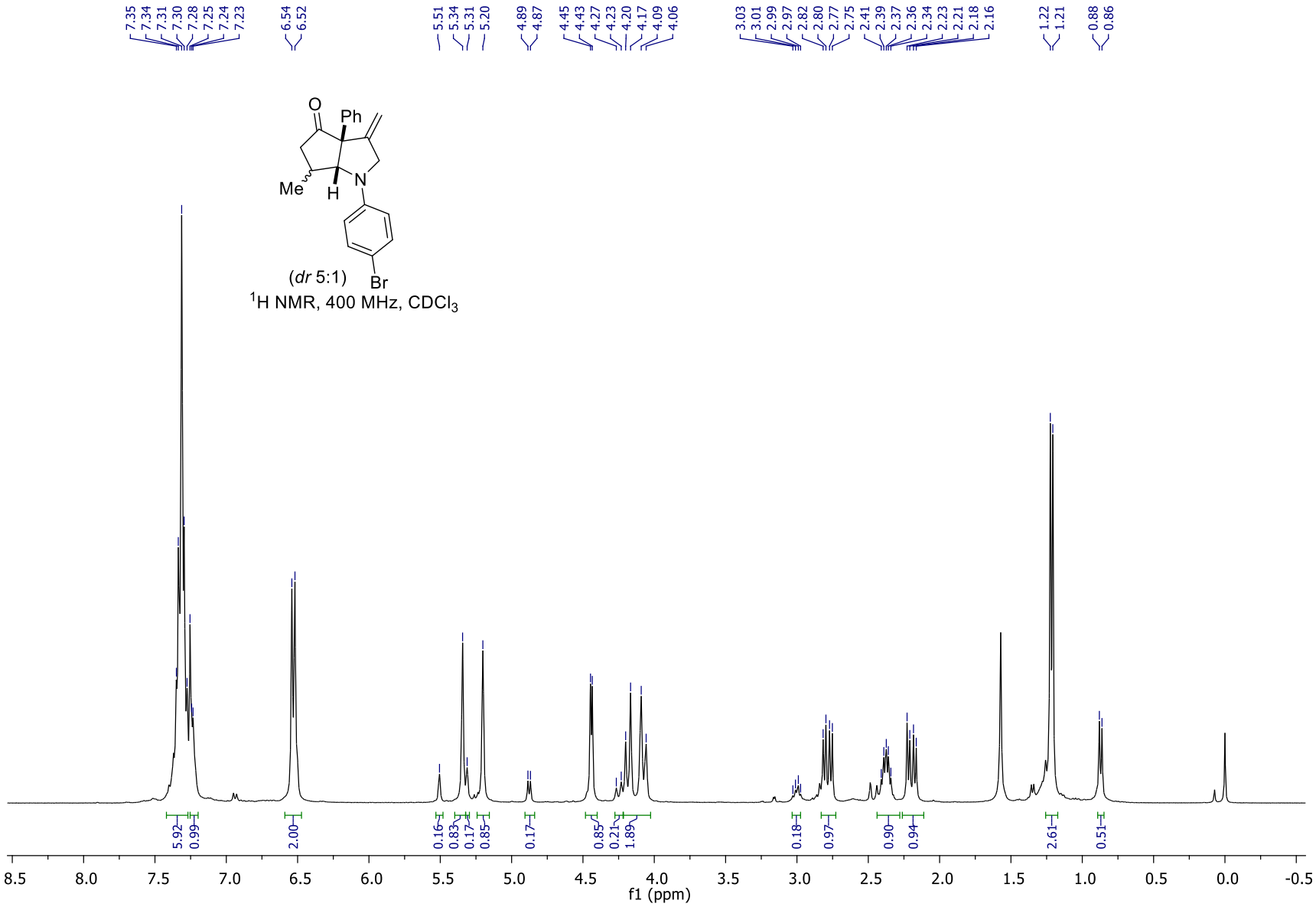
1-(4-Methoxyphenyl)-3-methyl-1,3a-diphenylhexahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (5)



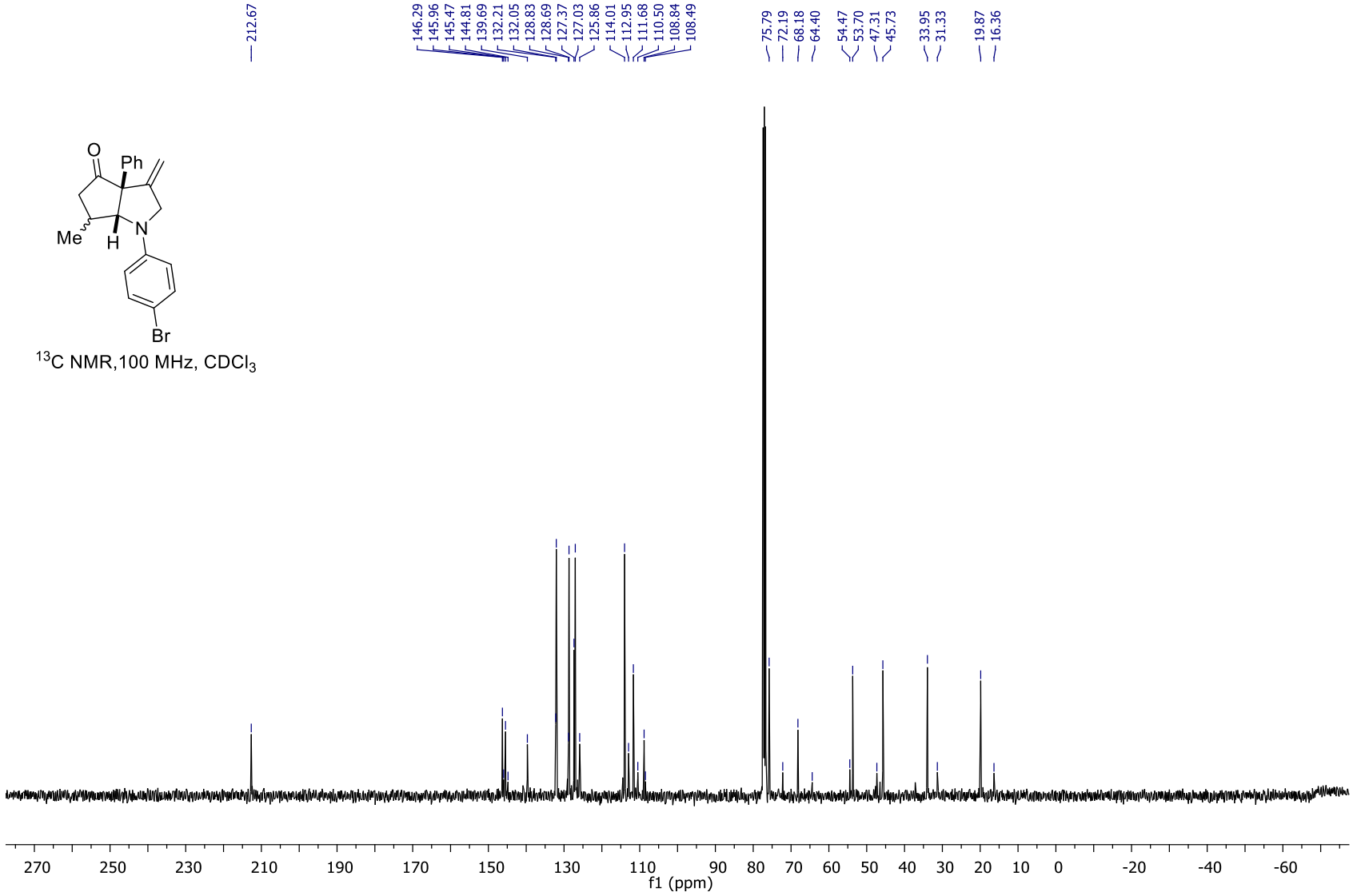
1-(4-Methoxyphenyl)-3-methyl-1,3a-diphenylhexahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (5)



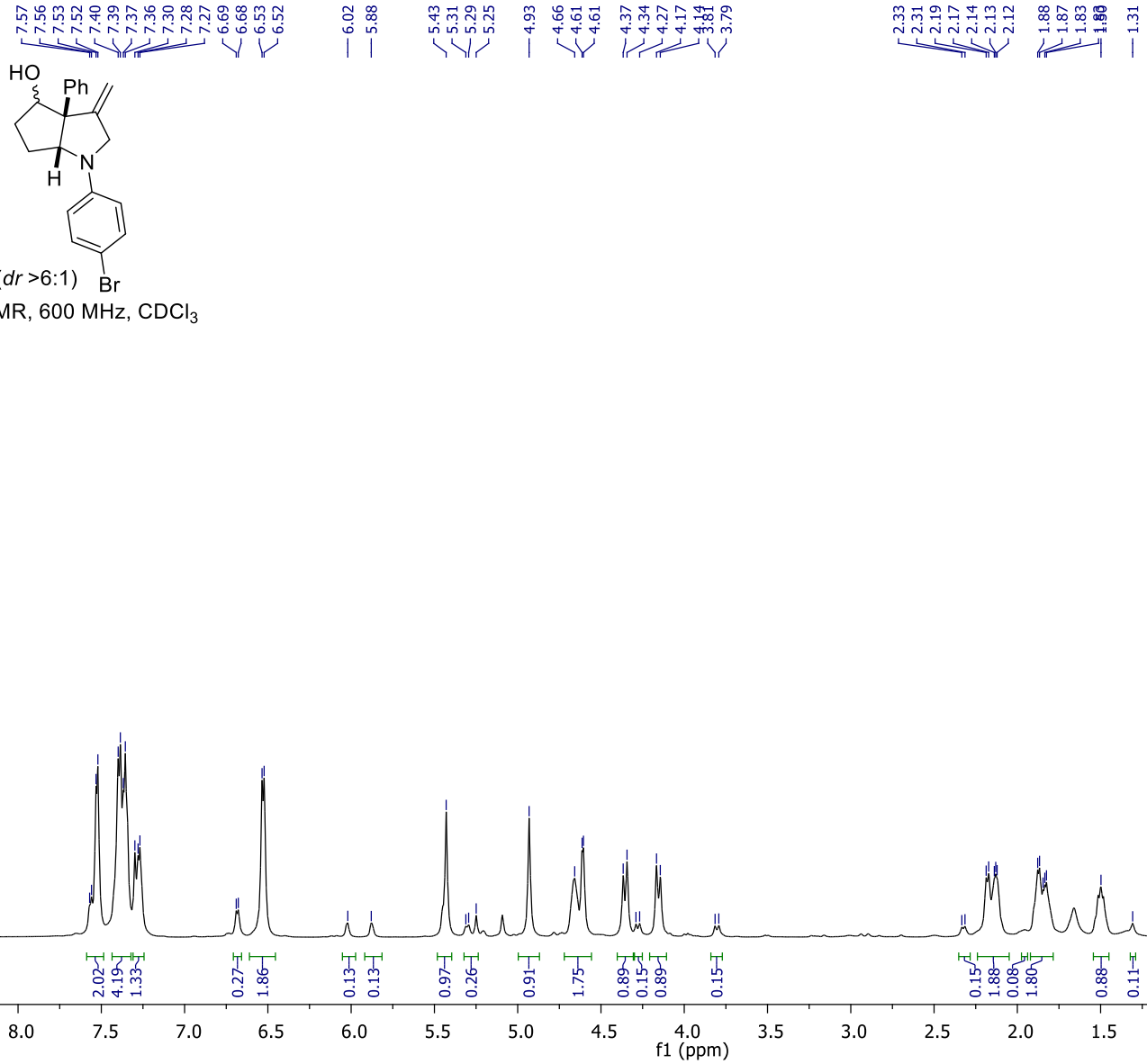
1-(4-Bromocyclohexa-1,5-dien-1-yl)-6-methyl-3-methylene-3a-phenylhexahydrocyclopenta[*b*]pyrrol-4(1*H*)-one (6)



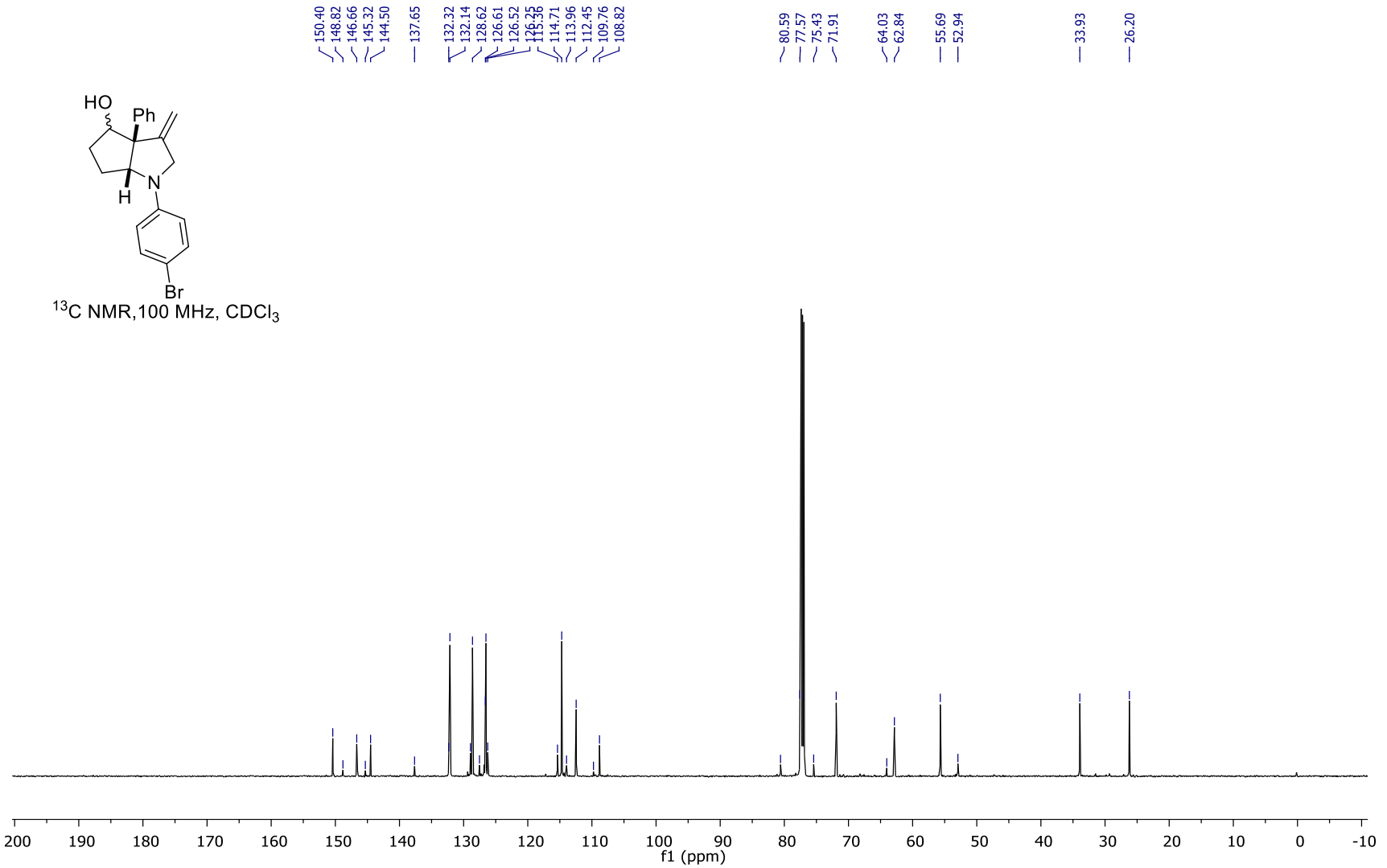
1-(4-Bromocyclohexa-1,5-dien-1-yl)-6-methyl-3-methylene-3a-phenylhexahydrocyclope nta[*b*]pyrrol-4(1*H*)-one (6)



1-(4-Bromophenyl)-3-methylene-3a-phenyloctahydrocyclopenta[*b*]pyrrol-4-ol (7)



1-(4-Bromophenyl)-3-methylene-3a-phenyloctahydrocyclopenta[*b*]pyrrol-4-ol (7)

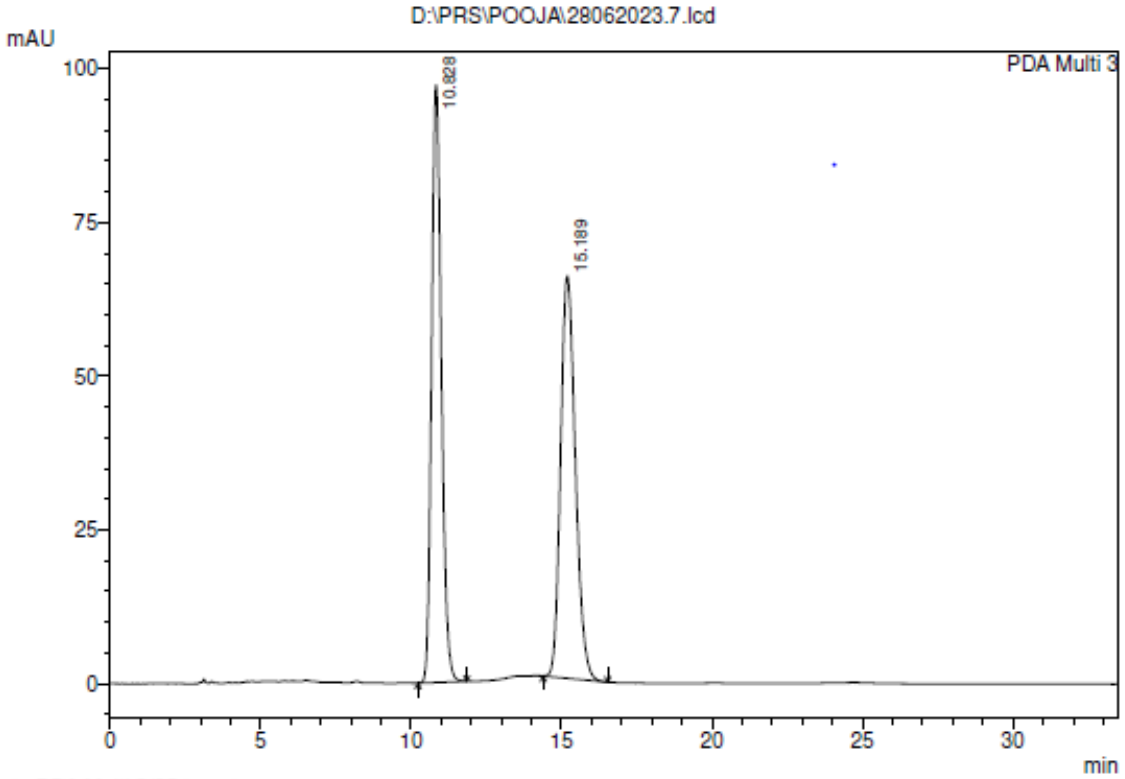


4. HPLC Analysis of Compound 4a

HPLC analysis conditions: EUROCEL-01 (250mmX4.6mm 5u) column, 15% IPA in hexanes (0.1% DEA), flow rate 1.0 mL/min, λ = 254 nm, tr (diastereomer 1) = 10.828 min, tr (diastereomer 2) = 15.189 min.

HPLC Report

<Chromatogram>



1 PDA Multi 3/254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.828	2197266	97154	49.525	59.759
2	15.189	2239434	65421	50.475	40.241
Total		4436700	162575	100.000	100.000

5. X-ray Crystallographic Data for Compounds 4f and 4o

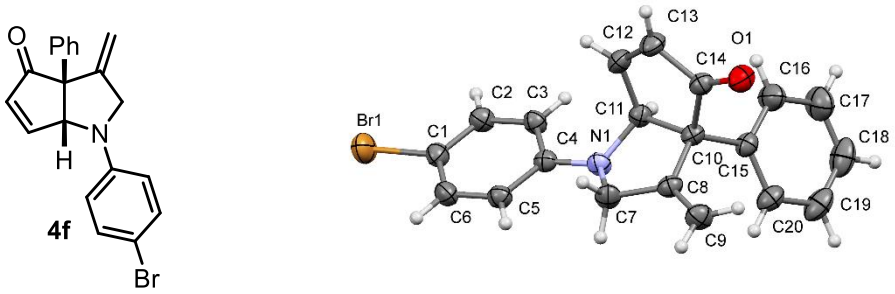


Figure S1. ORTEP diagram of **4f**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.

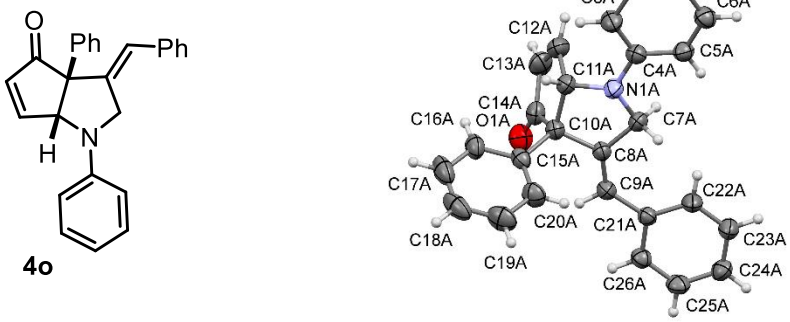


Figure S2. ORTEP diagram of **4o**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.

Crystallization of 4f: To a mixture of compound **4f** (20 mg) and dichloromethane (2 mL) in a culture vial and added five drops of hexanes. The vial was covered with perforated aluminium foil and left aside for 2 days at 25 °C for crystal growth. After slow evaporation of the solvent, pale yellow crystals were obtained.

Crystallization of 4o: To a mixture of compound **4o** (10 mg) and dichloromethane (1mL) in a culture vial and added three drops of hexanes. The vial was covered with perforated aluminium foil and left aside for 2 days at 25 °C for crystal growth. After slow evaporation of the solvent, colourless crystals were obtained.

X-ray data for the compound **4f** and **4o** were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å)

with ω-scan method [1]. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Integration and scaling of intensity data was accomplished using SAINT program [1]. The structure was solved by direct methods using SHELXS [2] and refinement was carried out by full-matrix least-squares technique using SHELXL [2]. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and U_{iso}(H) = 1.5U_{eq}(C) for methyl H or 1.2U_{eq}(C) for other H atoms].

Crystal structure determination of 4f

Crystal Data for 4f: $C_{20}H_{16}NOBr$ (M =366.25 g/mol): monoclinic, space group P21/c (no. 14), a = 10.887(2) Å, b = 13.619(3) Å, c = 11.857(2) Å, β = 110.116(3)°, V = 1650.7(6) Å3, Z = 4, T = 293.15 K, μ(MoKα) = 2.494 mm-1, Dcalc = 1.474 g/cm3, 19395 reflections measured (4.726° ≤ 2Θ ≤ 54.99°), 3785 unique (Rint = 0.0307, Rsigma = 0.0257) which were used in all calculations. The final R1 was 0.0385 (I > 2σ(I)) and wR2 was 0.1027 (all data). CCDC **2324040** contains supplementary Crystallographic data for the structure.

Crystal structure determination of 4o

Crystal Data for 4o: $C_{26}H_{21}NO$ (M =363.44 g/mol): monoclinic, space group Pn (no. 7), a = 8.577(4) Å, b = 16.525(7) Å, c = 29.330(12) Å, β = 98.477(8)°, V = 4112(3) Å3, Z = 8, T = 294.15 K, μ(MoKα) = 0.071 mm-1, Dcalc = 1.174 g/cm3, 39542 reflections measured (2.464° ≤ 2Θ ≤ 50°), 14481 unique (Rint = 0.0429, Rsigma = 0.0547) which were used in all calculations. The final R1 was 0.0440 (I > 2σ(I)) and wR2 was 0.1078 (all data). CCDC **2324045** contains supplementary Crystallographic data for the structure.

1. Bruker (2001). SAINT (Version 6.28a) & SMART (Version 5.625). Bruker AXS Inc., Madison, Wisconsin, USA.

2. Sheldrick G. M. (2015) Acta Crystallogr C71: 3-8.

6. References

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3. For hydrogenation procedure, see (a) P. R. Solanke, R. Cinsani, K. Nayani, P. S. Mainkar and S. Chandrasekhar, *Chem. Commun*., 2022, **58**, 5530–5533; for reduction procedure, see (b) S. Pearson, S. Fillery, K. Goldberg, J. Demeritt, J. Eden, J. Finlayson and A. Patel, *Synthesis (Mass.)*, 2018, **50**, 4963–4981.